

US EPA ARCHIVE DOCUMENT

REPORT

Implementation of the Pesticide Root Zone Model Groundwater (PRZM-GW) for Use in EPA's Pesticide Exposure Assessments

United States Environmental Protection Agency
Office of Pesticide Program, Environmental Fate and Effects Division

September 8, 2015

Prepared by:

Michael Barrett, Ph.D. Chemist
Rochelle Bohaty, Ph.D., Chemist
Mark Corbin, Branch Chief ERB6
James Cowles, Ph.D., Associate Division Director
Andrew Shelby, Environmental Engineer
James Wolf, PhD, Environmental Scientist
Dirk Young, Ph.D., Environmental Engineer

ABSTRACT

The Pesticide Root Zone Model Groundwater (PRZM-GW) was developed as a regulatory model to estimate pesticide concentrations in vulnerable groundwater sources as part of a North American Free Trade Agreement (NAFTA) to develop a harmonized groundwater modeling protocol.¹ The Office of Pesticide Programs implemented the use of PRZM-GW as an exposure model in 2012.² During a one-year evaluation period (January 2013 to December 2013), data were collected from 43 drinking water assessments and one registration review problem formulation completed by the Environmental Fate and Effects Division (EFED). These data were evaluated to determine 1) the effectiveness of PRZM-GW as a Tier 1 screen, 2) the impacts of the standard refinements, 3) a comparison of PRZM-GW estimated drinking water concentrations with the values estimated with the Screening In GROund Water (SCI-GROW), model and 4) risk assessment and risk management outcomes. The results of these analyses demonstrate that PRZM-GW is an effective and versatile model that can be used as a Tier 1 and Tier 2 risk assessment tool for estimating pesticide concentrations in groundwater.

¹ Baris, R., Barrett, M., Bohaty, R., Echeverria, M., Kennedy, I, Malis, G., Wolf, J., Young, D., Thurman, N. Final Report: *Identification and Evaluation of Existing Models for Estimating Environmental Pesticide Transport to Groundwater*; Health Canada, U.S. Environmental Protection Agency, October 15, 2012

² Brady, D. Approval of PRZM-GW for Use in Drinking Water Exposure Assessments, U.S. Environmental Protection Agency, December 11, 2012.

1. INTRODUCTION

The Pesticide Root Zone Model Groundwater (PRZM-GW) was developed as a regulatory model to estimate pesticide conservative concentrations in vulnerable groundwater sources as part of a North American Free Trade Agreement (NAFTA) to develop a harmonized groundwater modeling protocol.³ The Office of Pesticide Programs (OPP) implemented the use of PRZM-GW as an exposure model in 2012.⁴ This chapter describes how the model was implemented in the OPP.

1.1 BACKGROUND

After the passage of the Food Quality Protection Act (FQPA) of 1996, the EPA developed Screening In GROund Water (SCI-GROW)⁵ as a screening-level tool to estimate drinking water exposure concentrations in groundwater resulting from pesticide use.

SCI-GROW is an empirical model based on a linear best fit regression of the Relative Index of Leaching Potential (RILP)⁶, which considers the pesticide's application rate, mobility (K_{oc}) and persistence (aerobic soil metabolism half-life), and the 90-day maximum average groundwater concentrations observed in 13 prospective groundwater (PGW) studies⁷. The PGW studies were conducted at maximum allowable (single and yearly) application rates for pesticides that were determined, based on environmental fate properties, to have the potential to leach to groundwater. The studies were conducted in areas with shallow unconfined groundwater aquifers and regions where climatic conditions are expected to enhance groundwater vulnerability. The pesticide applications were made in year one of the study and groundwater samples were collected for approximately two to 10 years following the application year. Therefore, the SCI-GROW output represents the concentration (*i.e.*, 90-day average high concentration following one year of pesticide application) that might be expected in shallow aquifers under sandy soils. As a screening tool, SCI-GROW provides estimates of pesticides in groundwater, but it does not have the capability to consider variability in leaching potential of different soils, weather (including rainfall), cumulative yearly applications or depth to aquifer. If SCI-GROW based assessment results indicate that pesticide concentrations in drinking water exceed levels of concern, the ability to refine the assessment is limited.

In 2004, OPP initiated an evaluation of advanced methods for estimating pesticide concentrations in groundwater as part of the cumulative risk assessment of carbamate pesticides. OPP consulted with the FIFRA Scientific Advisory Panel (SAP) twice in 2005

³ Baris, R., Barrett, M., Bohaty, R., Echeverria, M., Kennedy, I., Malis, G., Wolf, J., Young, D., Thurman, N. Final Report: *Identification and Evaluation of Existing Models for Estimating Environmental Pesticide Transport to Groundwater*; Health Canada, U.S. Environmental Protection Agency, **October 15, 2012**

⁴ Brady, D., Approval of PRZM-GW for Use in Drinking Water Exposure Assessments, U.S. Environmental Protection Agency, **December 11, 2012**.

⁵ Barrett, M. *Initial Tier Screening of Pesticides for Groundwater Concentration Using the SCI-GROW Model*; U.S. Environmental Protection Agency: Washington, DC, 1997.

⁶ Or relative intrinsic leaching potentials The RILP is a function of aerobic soil metabolism and the soil-water partition coefficient (linear adsorption coefficient normalized for soil organic carbon content).

⁷ OPPTS 835.7100 Guidance for Prospective Ground-Water Monitoring Studies
<http://www.epa.gov/scipoly/sap/meetings/1998/october/grndwtr.pdf>

on the development of the groundwater conceptual model and the use of PRZM to implement the conceptual model.^{8,9} Concurrently, OPP and PMRA initiated a project under the auspices of the North America Free Trade Agreement (NAFTA) Technical Working Group on Pesticides to develop a harmonized approach to modeling pesticide concentrations in groundwater. The final NAFTA project report, which included an evaluation of PRZM-GW as a screening-level groundwater exposure model, recommended PRZM-GW as the harmonized tool for assessing pesticide concentrations in groundwater. PRZM-GW is a one-dimensional, finite-difference model that estimates the concentrations of pesticides in groundwater. It accounts for pesticide fate in the crop root zone by simulating pesticide transport and degradation through the soil profile after a pesticide is applied to an agricultural field. PRZM-GW permits the assessment of multiple years of pesticide application (a SCI-GROW limitation as noted in the SAPs) (up to 100 years) on a single site. Six standard scenarios, each representing a different region known to be vulnerable to groundwater contamination, are available for use with PRZM-GW. PRZM-GW output values represent pesticide concentrations in a vulnerable groundwater supply that is located directly beneath a rural agricultural field.

OPP implemented the use of PRZM-GW as an exposure model in 2012.¹⁰

1.2 IMPLEMENTATION SUMMARY

For one year, EFED scientists estimated Tier 1 drinking water concentrations (EDWCs), using the models PRZM-GW (Version 1.0) and SCI-GROW (Version 2.3). Although chemical specific fate parameters were considered as model inputs for both models, the specific input values varied between the two models. A comparison of the chemical input values included in the input parameter guidance for PRZM-GW and SCI-GROW are provided in **Table 1.1**.

Table 1.1. Tier 1 PRZM-GW and SCI-GROW Chemical Input Comparison

Parameter (units)	PRZM-GW Input Value ^a	SCI-GROW Input Value ^b
Application Date(s) (day/month/year)	Use the maximum number of applications and minimum application interval for the modeled use.	Not considered
Application Rate (kg a.i. ha ⁻¹)	Use the maximum application rate allowed per application for the modeled use.	Use the maximum single application rate allowed on the label for the modeled use (<i>i.e.</i> , lb a.i./A).
Number of Applications	Use the maximum number of applications and minimum application interval for the modeled use.	Use the maximum number of applications allowed on the label for the modeled use.
Application Method	CAM 1 (soil) or 2 (foliar)	Not considered

⁸ U.S. Environmental Protection Agency. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Advisory Panel: N-Methyl Carbamate Pesticide Cumulative Risk Assessment: Pilot Cumulative Analysis, February 15-18, 2005 (a), 2005-01, Docket Number: OPP-2004-0405.

⁹ U.S. Environmental Protection Agency. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Advisory Panel: Preliminary N-Methyl Carbamate Cumulative Risk Assessment, August 23-26, 2005 (b), 2005-04, Docket Number: OPP-2005-0172

¹⁰ Brady, D., Approval of PRZM-GW for Use in Drinking Water Exposure Assessments, U.S. Environmental Protection Agency, December 11, 2012.

Hydrolysis Half-life (days)	Use the relevant hydrolysis half-life for the aquifer pH.	Not considered
Soil Half-life (days)	Use aerobic soil metabolism half-life adjusted to 25 °C.	If three or less aerobic soil metabolism half-life values are available, use the mean value. If there are four or more half-lives available, use the median value. If there is more than a five-fold difference, make note of the range.
Pesticide Partition or Distribution Coefficients (mL/g or cm ³ g ⁻¹)	Mean of the K _{OC} or K _d values If sorption is correlated with organic carbon content, use the K _{OC} values. If sorption is not correlated with organic carbon content, use the K _d values. It is assumed that K _F = K _d	If the partition coefficients normalized for organic carbon content (K _{OC} or K _{FOC}) show greater than a three-fold variation, use the lowest value. If not, then use the median value. It is assumed that K _F = K _d
a. U.S. Environmental Protection Agency, Office of Pesticide Programs, Environmental Fate and Effects Division <i>Guidance for Selecting Input Parameters for Modeling Pesticide Concentrations in Groundwater Using the Pesticide Root Zone Model</i> , Version 1.0, October 15, 2012 b. U.S. Environmental Protection Agency, Office of Pesticide Programs, Environmental Fate and Effects Division <i>Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides</i> , Version 2.1, October 22, 2009		

For Tier 1 assessments, the results from the model, either SCI-GROW or PRZM-GW, which provides the highest EDWCs were incorporated along with surface water EDWCs to determine a reasonable upper bound estimate of pesticide concentrations in drinking water. These EDWCs were used by the Health Effects Division (HED) in the dietary risk assessment according to the decision tree provide in **Figure 1.1**. PRZM-GW was used as a Tier 2 assessment tool when groundwater modeling refinements were necessary (**Figure 1.2**).

For Tier 1 drinking water assessments, PRZM-GW simulations were completed using all six standard scenarios¹¹ with a 30-year meteorological data file for each assessed crop/use site. If the “throughputs¹²” value for a model run is less than one, modeling should be repeated with the appropriate extended weather file. An extended weather file contains the same weather as the standard 30-year weather file and allows the user to run the simulation for up to 100 years in order to observe breakthrough. For each crop/use site, the highest daily peak concentration was reported for short-term exposure (acute), while the post-breakthrough average concentration was reported for longer term exposures (chronic and cancer). In addition, the average simulation breakthrough time was provided for characterization.

¹¹ Florida Citrus, Florida Potato, Wisconsin Corn, Georgia Peanuts, North Carolina Cotton, and Delmarva Sweet Corn

¹² The estimated pore volumes/retardation factor that occurs in the simulation.

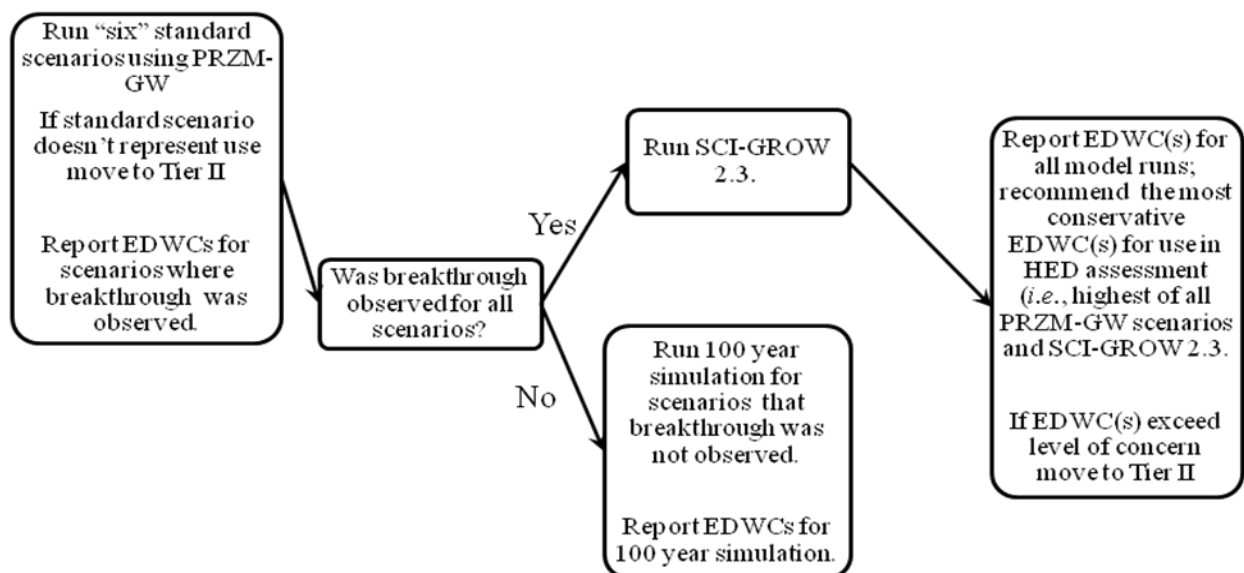


Figure 1.1. Tier 1 Groundwater Exposure Assessment Process Diagram

Tier 2 assessment for groundwater is implemented if Tier 1 exceeds surface water EDWCs and a potential exposure concern is noted. For Tier 2 drinking water assessments, only PRZM-GW was recommended for use as SCI-GROW is only a screening-level tool and does not have refinement capabilities. Several refinement strategies were recommended in the PRZM-GW user guidance. The strategies included: development of representative scenarios, consideration of environmental fate parameters not considered in the Tier 1 simulations such as subsurface transformation or sorption, examination of use assumptions, including annual application retreatment, the impact of well setbacks (if not already specified on the label), exploration of duration of exposure that are representative of the exposure duration of concern. The most conservative refined EDWCs (surface water or groundwater) were recommended for use in the human health dietary exposure assessment.

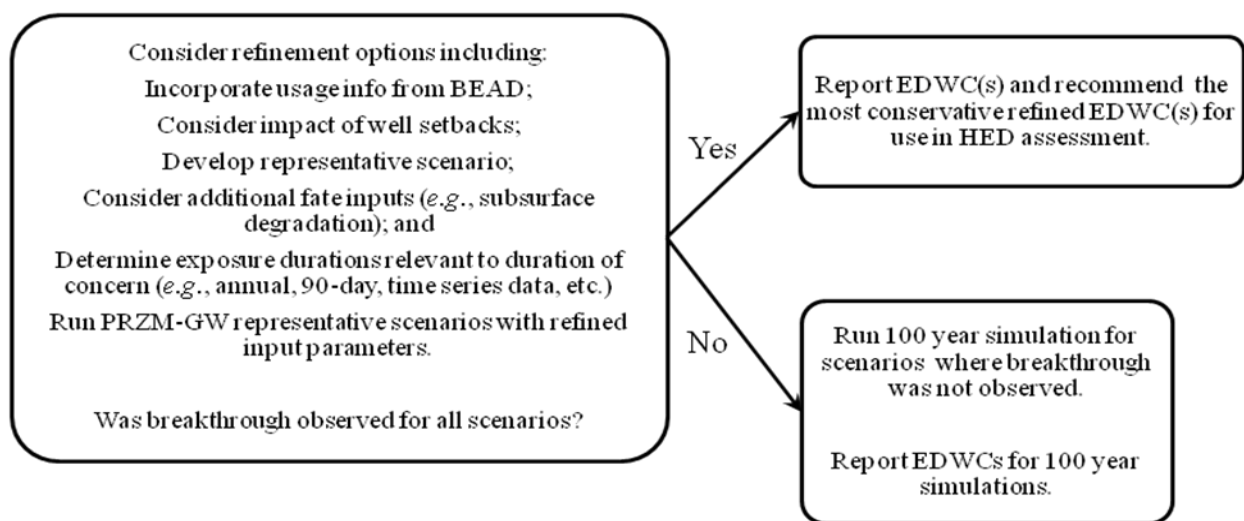


Figure 1.2. Tier 2 Groundwater Exposure Assessment Process Diagram

1.3 IMPLEMENTATION EVALUATION AND ADDITIONAL ANALYSES

During the evaluation (January 2013 to December 2013) period, EFED's PRZM Groundwater Team collected data on risk assessment and management outcomes. The primary goal of the evaluation was to determine if PRZM-GW is an effective Tier 1 screening model as implemented. A total of 43 drinking water assessments were completed by EFED for 42 different active pesticide ingredients during the evaluation period. In addition, for one registration review problem formulation, the groundwater model was run as a screen to determine if additional data were needed to support the registration review risk assessment. This analysis was submitted to the groundwater team for inclusion in the implementation evaluation. A list of chemicals included in this evaluation is provided in **APPENDIX A**. Data collected from these assessments were evaluated to determine:

- a. how often Tier 1 PRZM-GW or SCI-GROW EDWCs were selected for use in the dietary risk assessment,
- b. what modeling approach was used [*i.e.*, parent or total toxic residue (total residue, residue summation or formation/decline methods)]¹³,
- c. how often Tier 1 modeling estimates were refined,
- d. what refinement options were considered, including those considered by EFED as well as HED, and

All the data were compiled in an Excel spreadsheet and are provided in **APPENDIX B**. The results of the analysis are presented in the subsequent chapters. **Chapter 2** focuses on the effectiveness of PRZM-GW as a Tier 1 screen (points a, b, c above). **Chapter 3** explores the impacts of standard refinements (point d above) and presents the risk assessment conclusions. Additional analyses were completed that compared the PRZM-GW EDWCs with SCI-GROW EDWCs. These analyses are presented in **Chapter 4**. Updates were made to the standard scenarios to correct an error in the water holding capacity. An evaluation of the updated scenario was completed and the results are presented in **Chapter 5**.

¹³ U.S. Environmental Protection Agency, Ruhman, M., Hetrick, J., Jones, R. Guidance for Modeling Pesticide Total Toxic Residues, draft document

2. ASSESSMENT OF PRZM-GW AS A TIER 1 REGULATORY SCREENING MODEL

This chapter focuses on the evaluation of PRZM-GW as implemented in Environmental Fate and Effects Division (EFED) as a Tier 1 tool for estimating pesticide concentrations in drinking water to support the Office of Pesticides Regulatory actions.

2.1 METHOD OVERVIEW

Data were collected from all drinking water assessments (DWAs) completed by the EFED during 2013 (January through December). Data collected included: 1) how often Tier 1 PRZM-GW (Version 1.0) or SCI-GROW (Version 2.3) EDWCs were selected for use in the dietary risk assessment, 2) what modeling approach was used, and 3) how often Tier 1 modeling estimates were refined. These data were compiled in an excel spreadsheet and are provided in **APPENDIX B**.

The data were collected to determine if PRZM-GW is an effective Tier 1 screen as implemented in EFED. In defining an effective screen, EFED used the criteria that EDWCs should not be overly conservative and require frequent refinements. Overly conservative estimates could result in a large commitment of EFED and/or HED resources. Based on cursory data provided to EFED by the Health Canada Pest Management Regulatory Agency (PMRA), groundwater modeling refinements using PRZM-GW may be needed approximately 20% of the time. Prior to the implementation of PRZM-GW, PMRA used LEACHM to estimate pesticide concentrations in groundwater. The LEACHM¹⁴ model is conceptually similar to PRZM-GW, and, therefore, exposure estimates were expected to be similar between the two models. For this analysis, the criteria defining an effective screen was selected to be 80:20, meaning an effective Tier 1 screen would require refinements less than 20% of the time. If refinements were necessary more than 20% of the time, additional analysis of the data would be conducted to determine if improvements could be made to increase the effectiveness of PRZM-GW as a Tier 1 screen to reduce the resource burden at the Tier 1 screening level.

2.2 RESULTS AND DISCUSSION

Data were collected from 43 DWAs, representing 42 different pesticide active ingredients. The active ingredients included in this analysis are provided in **APPENDIX A**.

Of the 43 DWA examined, only four recommended the use of a SCI-GROW derived EDWCs for comparison with surface water EDWCs. A comparison of the model input values used in the value modeling runs are provided in **Table 2.1**. In all but one case, the input values used in the two different models were different and likely resulted in the difference in the EDWCs. However, for one chemical (listed as Chemical 8 in **APPENDIX A**), the model input values were exactly the same for both models with the exception that PRZM-GW was also able to

¹⁴ Hutson, J.L. (2003). Leaching Estimation and Chemistry Model (LEACHM): A process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone. Research Series No. R03-1, pp. 140 pp.

consider hydrolysis. The difference in the EDWCs is the result of using a high sorption value ($K_{oc} = 72,000 \text{ mL/g}_{oc}$). SCI-GROW is not recommended for modeling chemicals with high sorption values ($K_{oc} \geq 10,000 \text{ mL/g}_{oc}$). SCI-GROW also contains a default lower bound value, while PRZM-GW does not. Therefore, the EDWCs derived using SCI-GROW was the result of using a high sorption value and the model defaulting to the lower bound. One additional drinking water assessment that was conducted for Chemical 36 in **APPENDIX A** contained modeling runs where SCI-GROW estimated higher groundwater concentrations than PRZM-GW. While the EDWCs for both parent compound and one transformation product were estimated to be higher using SCI-GROW, the EDWCs for another (more terminal transformation product) were higher using PRZM-GW. Therefore, the recommended EDWCs for use in the dietary risk assessment were derived using PRZM-GW.

Table 2.1. Comparison of Model Input and Output Values for Those Chemicals Where SCI-GROW EDWCs Were Higher than PRZM-GW

Chemical Identification ^a	Hydrolysis Half-life (days)	Aerobic Soil Metabolism (days)		Sorption Value (K_{oc}) (mL/g_{oc})		Modeling Approach	Comment
	PRZM-GW	SCI-GROW	PRZM-GW	SCI-GROW	PRZM-GW		
Chemical 8	155	114.8	114.8	72000	72000	TTR-TR	SCI-GROW lower bound
Chemical 33	stable	465.5	400	18,300	47,513	Parent	SCI-GROW lower bound
Chemical 34	stable	1,628	6,833	13	24	TTR-TR	Different ASM values
Chemical 36 (parent) ^b	13.1	0.25	0.210	237	4.39 (k_d)	Parent-RS	Different sorption values
Chemical 36 (transformation product) ^b	stable	0.035	0.083	27	55.0	Degradate-RS	Degradate of Chemical 36 Different sorption values
Chemical 38	stable	796	796	1085	12.7 (k_d)	parent	Different sorption values
a. See APPENDIX A for chemical name. b. Input values not provided in the table for the transformation products that resulted in PRZM-GW EDWCs greater than SCI-GROW EDWCs. Total Toxic Residues (TTR) – Total Residue (TR) or Residue Summation (RS) (see footnote 13)							

Of the 43 DWAs examined, eight chemicals failed the Tier 1 screen (*i.e.*, Tier 1 surface water or groundwater EDWCs exceeded the level of concern for drinking water). Of the eight chemicals, five were based on groundwater modeling. (See **Table 2.2** for model input values used in PRZM-GW modeling runs). The other DWAs failed the screen based on surface water modeling. For all five of the assessments that Tier 1 EDWCs exceeded the risk concern for groundwater, the EDWCs were derived using PRZM-GW.

Table 2.2. Comparison of Model Input for Those Chemicals Where Tier 1 PRZM-GW EDWCs Triggered Risk Concerns

Chemical Identification ^a	Hydrolysis Half-life (days)	Aerobic Soil Metabolism (days)	Sorption Value (K _{oc}) (mL/g _{oc})	Modeling Approach	Endpoint of Concern	Previous Drinking Water Concern?	Comment
Chemical 3	3660	132	44	TTR-TR	Chronic	No	New toxicity data received – no longer considered as triggering risk at Tier 1
Chemical 5	stable	392	336	TTR-TR	Cancer	No	New chemical
Chemical 7	0	314	11.5	TTR-TR	Cancer	Yes	Increased number of yearly applications requested
Chemical 16	315	1030	23.5	TTR-TR	Cancer	No	Incorrect input values used in previous assessments; correct input values would have indicated drinking water concern
Chemical 40	stable	97.6	41	Parent	Cancer	Yes	New use
See APPENDIX A for chemical name. Input values not provided in the table for the transformation products that resulted in PRZM-GW EDWCs greater than SCI-GROW EDWCs. Total Toxic Residues (TTR) – Total Residue (TR) or Residue Summation (RS) (see footnote 13)							

The analysis also showed that for four of the five assessments in which risk was identified by the Tier 1 screen, four of those assessments were based on a total toxic residue modeling approach. This modeling strategy assumes that all identified residues of toxicological concern have similar physical, chemical, and partitioning characteristics. Application rates for the parent pesticide are used to represent the total mass loading of pesticide and its degradation product(s). This modeling approach does not consider temporal occurrence of degradation products.

The toxicological endpoint of concern identified in all five assessments were based on a longer term exposure duration (*i.e.*, chronic or cancer). For one of the chemicals initially flagged by the Tier 1 screen, new toxicity data were submitted to the EPA. This toxicity information resulted in modifications to the dietary exposure assessment and corresponding toxicity endpoint such that PRZM-GW derived EDWCs did not result in risk concern. While consideration of new toxicity data is not considered a refinement, had this data not been submitted to the EPA, risk would have been identified as part of the Tier 1 screening process.

2.3 SUMMARY

Of 43 DWA completed in 2013, only four assessments, which recommended the use of a PRZM-GW derived EDWC in the human health assessment, resulted in the identification of a potential risk concern at the Tier 1 screening level. This analysis demonstrates that PRZM-GW, implemented as a Tier 1 screen, is not a resource burden. In fact, at the Tier 1 level, risk concerns were identified about half as often as anticipated. However, this analysis shows that when Tier 1 risks are identified using PRZM-GW, it is likely that a total toxic residues approach and/or a longer term exposure duration was considered.

3. EVALUATION OF STANDARD PRZM-GW REFINEMENTS AND SUMMARY OF RISK ASSESSMENT AND RISK MANAGEMENT OUTCOMES

This chapter focuses on the evaluation of standard refinements provided in the Guidance for Using PRZM-GW in Drinking Water Exposure Assessment¹⁵ document. This analysis was completed to determine if any of the refinements should be considered as part of a Tier 1 analysis to increase the efficiency of the screening process. In addition, refinements to the dietary risk assessment conducted by the Health Effects Division (HED) were also considered as well as the risk management outcomes to date.

3.1 METHOD OVERVIEW

All 43 drinking water assessments (DWAs) were examined as part of this analysis; however, most of the focus of this chapter is on the four DWAs identified in the previous chapter as a potential risk concern at the Tier 1 screening level. The assessments were examined further to determine what refinement strategies included in the Guidance for Using PRZM-GW in Drinking Water Exposure Assessment were employed and the results of the refinements. Standard refinements include: development of representative scenarios, consideration of environmental fate parameters not considered in the Tier 1 simulations such as subsurface transformation or sorption, examination of use assumptions including annual application retreatment, the impact of well setbacks (if not already specified on the label), exploration of duration of exposure that are representative of the exposure duration of concern. Note that the DWA completed for Chemical 3 was not further examined because it was determined to no longer trigger risk concern at the Tier 1 level based on new toxicity data.

In addition, refinements to the dietary risk assessment conducted by the HED were also captured as part of this analysis.

3.2 RESULTS AND DISCUSSION

Scenario Development

No new scenarios were developed as part of the implementation phase of PRZM-GW. Of the four drinking water assessments evaluated further, only one considered a site-specific scenario, and in this case one of the standard scenarios represented the intended use site (citrus). Therefore, the development of a new scenario was not needed.

¹⁵ U.S. Environmental Protection Agency, Baris, R., Barrett, M., Bohaty, R., Echeverria, M., Wolf, J., Young, D. Guidance for Using PRZM-GW in Drinking Water Exposure Assessment, October 15, 2012

Table 3.1. Tier 2 Refinements Considered

Chemical Identification ^a	Aquatic Exposure Refinements	Dietary Exposure Refinements	Mitigation Options Explored	Did Refinements or Mitigation Resolve Risk Concern?
Chemical 5	Site-specific scenario considered (one of the six standard scenarios reasonably represented the intended use site)	Anticipated residues using field trial data; expected crop treated data	None	No
Chemical 7	None	None	Alternative Use	No
Chemical 16	Well setback	Anticipated residues using field trial data; expected crop treated data	Alternative Use	No
Chemical 40	Utilized volatility routine; considered additional well setbacks as well as examined input values used in well setback calculations	None	None	No
See APPENDIX A for chemical name.				

Subsurface Transformation

Based on the current conceptual model implemented in PRZM-GW, the chemical transformation rate in the subsurface is equal to or greater than (considering aerobic soil metabolism in the top one meter) the rate of hydrolysis. At the Tier 1 level, the only transformation considered below a depth of one meter is hydrolysis. For this reason, hydrolysis is a highly sensitive input parameter for PRZM-GW. While the guidance for using PRZM-GW includes hydrolysis as part of Tier 1 simulations, hydrolysis is often considered stable. This is reflective of the guideline hydrolysis study (OCSPP 835.2120) design. The study is designed as a 30-day abiotic study, and in general when the DT50 is not observed during the course of the study, the compound is characterized as stable. When necessary, the study may be used to determine if a statistically significant amount of hydrolysis is observed and the rate of hydrolysis even if the corresponding half-life values are greater than 30 days. If a statistically significant rate of degradation cannot be determined, the compound should be modeled as stable in the absence of additional data. Additional data that may be useful include a longer hydrolysis study or a hydrolysis study conducted at a higher temperature.

It should be noted that the guideline hydrolysis study also only captures abiotic hydrolysis and may not capture other mechanisms of subsurface hydrolysis such as soil surface catalyzed hydrolysis. This outcome is supported in the literature. For example, atrazine has been shown to undergo hydrolytic degradation in groundwater.¹⁶ Use of this subsurface hydrolysis rate in PRZM-GW modeling results in EDWCs that are in reasonable agreement (**Table 3.2**) with groundwater monitoring data when the uncertainties associated with the monitoring data such as well depth and sampling frequency as well as precision of the model (generally model estimates are considered reasonable within an order of magnitude) are considered.

¹⁶ Navarro, S., Vela, N., Giménez, M. J., Navarro, G. Persistence of Four s-triazine Herbicides in River, Sea and Groundwater Samples Exposed to Sunlight and Darkness Under Laboratory Conditions, Science of the Total Environment, 2004, 329, 87-97.

Table 3.2. PRZM-GW EDWCs for Total Chlorotriazines in Groundwater

USGSRP REPORT GW-EDW for Total Chlorotriazines in Groundwater					
Pesticide	Scenario	Annual Application Rate (lb a.i./A)	Peak	Breakthrough Average	Highest Groundwater Monitoring Data
Atrazine	FLC	2.5	201	124	16.6 (USGS) 8.5 (CDPR)
	FLP	2.5	151	94	
	GAP	2.5	47	24	
	DEL	2.5	204	144	
	NCC	2.5	88	48	
	WIC	2.5	129	96	
	FLC	10	782	543	
Delmarva Corn (DEL), Florida Citrus (FLC), Florida Potato (FLP), Georgia Peanut (GAP), North Carolina Cotton (NCC), and Wisconsin Corn (WIC) United States Geological Survey (USGS) California Department of Pesticide Regulation (CDPR) Model input values used for modeling total chlorotriazine residues: aerobic soil metabolism half-life value of 564 day; organic carbon partition coefficient of 31.3 mL/g _{oc})					

While subsurface degradation studies are not routinely submitted to the EPA as part of the pesticide registration process, if transformation data are available for a given pesticide in subsurface materials, these data may be used to refine PRZM-GW modeling. Nevertheless, no additional subsurface transformation were considered in the Tier 2 simulations conducted during the implementation phase of PRZM-GW as suitable data were not available for the chemicals assessed. Pesticide degradation may be slow and is generally expected to slow with increasing depth degradation if it is still possible. In conjunction with observed field data and hydrolysis data, it is justifiable to use other data sources such as aerobic soil and aquatic metabolism data as lines of evidence to estimate a dissipation half-life value in subsurface materials. Shallow, unconfined aquifers have the potential to exhibit conditions conducive to aerobic metabolism though the extent and prevalence of this type of degradation is uncertain.

Subsurface Sorption

Time Dependent Sorption and Nonlinear Isotherms

Several comments have been received from registrant groups regarding incorporation of both non-equilibrium (time-dependent) sorption and nonlinear sorption into the modeling process. EFED considered both processes and concluded that inclusion of non-equilibrium sorption would make the model more complicated while adding little to reduce uncertainty. In addition, it is the opinion of EFED that studies of sufficient quality are not yet available to derive the necessary parameters for non-equilibrium modeling. On the other hand, consideration of nonlinear isotherms may be possible with currently available studies, and EFED is considering including Freundlich isotherms in future PRZM-GW releases.

Use Assumptions

The Biological and Economic Analysis Division (BEAD) was asked to investigate the use assumptions included in PRZM-GW Tier 1 modeling (*i.e.*, 30 or a 100 years of repeated application). While a formal document was not prepared by BEAD, BEAD was not able to identify alternative use scenarios by use site or chemical/pesticide class. BEAD recommended that yearly retreatment be considered on a chemical specific basis. Sources of use information include BEAD, California Department of Pesticide Regulation, etc. for specific chemicals. Use restriction may also be included on pesticide labels. For example, one of the 43 DWA examined considered application retreatment every other year as part of Tier 2 PRZM-GW simulations. This analysis resulted in label language restricting the use of the pesticides to once every 24 months.

Well Setback

Well setbacks (equation shown below) were considered in two of the four assessments requiring refinement. A well setback increases the amount of time for a chemical to reach the wellhead thereby increasing the amount of time for dissipation and ultimately reducing the pesticide concentration at the well. For one of these compounds, a well setback is included on the label and would not be considered a refinement; however, larger well setback distances were also considered as part of a monitoring data comparison. The guidance for using PRZM-GW provides a well-setback equation; however, little information is provided on parameterizing the equation.

$\frac{C}{C_0} = \exp\left(-\frac{L}{v}k\right)$	<p>C = concentration at well C₀ = concentration at point of application L = well setback distance [feet] v = lateral groundwater velocity [feet/day] k = dissipation rate in aquifer [day⁻¹]</p>
--	--

The well setback equation is highly sensitive to small changes in the lateral groundwater velocity (v) and the aquifer degradation rate (k) or sorption. For instance, if either the groundwater velocity or the degradation rate is changed by a factor of two, estimated concentrations at a given well setback distance are changed by a factor of 38. Groundwater flow velocities can vary greatly as the U.S. Geological Survey indicates that a lateral groundwater velocity of one foot per day or greater is high, while groundwater velocities can be as low as one foot per year or one foot per decade.¹⁷ This suggests that groundwater flow varies widely across the country and when coupled with degradation, which is also known to vary across the landscape, results in a large amount of uncertainty in the EDWCs when using this approach.

Volatility Routine

One of the compounds that triggered a risk concern at the Tier 1 screening level is volatility. To address this potential dissipation pathway for this compound, a volatility routine was added to PRZM-GW. Input values considered in the volatility routine include diffusion in air (cm²/day),

¹⁷Alley, W. W., Reilly, T. E., Franke, O.L., Sustainability of Ground-Water, U.S. Geological Survey—Circular 1186, 1999, http://pubs.usgs.gov/circ/circ1186/html/gen_facts.html

enthalpy (kcal/mol), and Henry's Law Constant. In addition, the standard scenarios needed to be updated to include canopy height (see **Chapter 5**).

Scenario Characterization

During the initial evaluation of PRZM-GW as an exposure tool, many questions were raised about the representation of the EDWCs derived using PRZM-GW, including the location and population that uses the represented vulnerable groundwater sources as source drinking water. In the absence of developing a national-scale groundwater vulnerability assessment map, a United States Geological Survey (USGS) publication¹⁸ was examined to provide context to the spatial extent of shallow unconfined aquifers or highly vulnerable groundwater sources that may be used as source drinking water (represented by the conceptual model implemented in PRZM-GW). This publication examined the vulnerability of shallow groundwater and drinking water wells to nitrate contamination and developed a predictive model for assessing the relative vulnerability across the contiguous states. Nitrate is considered the most widespread contaminant in groundwater. It is both soluble and mobile as well as used heavily in agricultural settings, making it a reasonable surrogate for a national groundwater vulnerability assessment for characterizing the conceptual model and standard scenarios used in the PRZM-GW model. **Figure 3.1** provides an overlay of the six PRZM-GW standard scenarios¹⁹ and the nitrate vulnerability map developed by the USGS. This overlay confirms that the six PRZM-GW standard scenarios fall within regions where groundwater is highly susceptible to nitrate contamination. This overlay also highlights regions such as Nebraska, California, and Washington, which have vulnerable groundwater sources that may not be reasonably represented by one of the current scenarios because of differences in weather, agronomic practices, soil properties, etc. Nevertheless, the current scenarios are expected to provide reasonable upper bound estimates for pesticide concentrations for vulnerable groundwater sources.

¹⁸ Nolan, B. T., Hitt, K. J. Vulnerability of Shallow Groundwater and Drinking-Water Wells to Nitrate in the United States, *Environ. Sci. Technol.* 2006, *40*, 7834-7840

¹⁹ Delmarva Corn (12/23/13), Florida Citrus (12/23/13), Florida Potato (12/23/13), Georgia Peanut (12/23/14), North Carolina Cotton (12/23/13), and Wisconsin Corn (12/23/13)

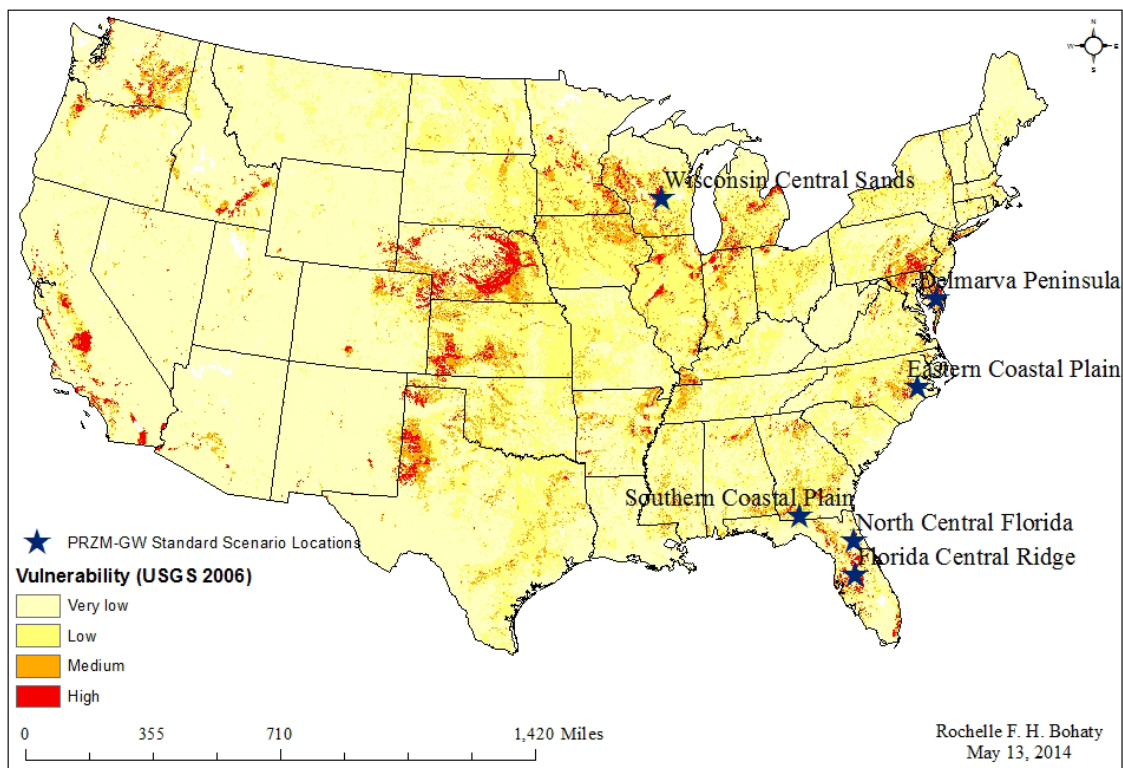


Figure 3.1. Groundwater Vulnerability Map Overlaid with PRZM Groundwater Scenario Locations

This publication also contains information on the use of shallow unconfined aquifers as source drinking water. Up to a million people in the United States use highly vulnerable (10 m and 50 m simulated well depths considered) groundwater sources for source drinking water. These values were derived by using GIS to delineate the population on wells serving four or fewer housing units and is based on the 1990 census of population and housing data.

Several sources were examined to characterize the potential population that may use vulnerable groundwater sources as drinking water. Another USGS publication, one that contains a five-year review of water use in the U.S., indicates that 14% (42,900,000) of the US population derives their drinking water from self-supplied sources with groundwater as the dominant source.²⁰

There is no national data set on the percentage of private drinking water wells that are in shallow unconfined aquifers. However, to provide context, another USGS publication was reviewed that provides information on private domestic wells in the Virginia Coastal Plain.²¹ In this study (which did not include contaminant monitoring), approximately 25% of wells in the Virginia

²⁰ Kenny, J.F., Barber, N.L., Hutson, S.S., Linsey, K.S., Lovelace, J.K., and Maupin, M.A., 2009, Estimated use of water in the United States in 2005: U.S. Geological Survey Circular 1344, 52 p.
<http://pubs.usgs.gov/circ/1344/pdf/c1344.pdf>

²¹ Pope, J.P. *et al.* 2007. Private Domestic-Well Characteristics and the Distribution of Domestic Withdrawals Among Aquifers in the Virginia Coastal Plain. U.S. Geological Survey. Groundwater Resources Program.
<http://pubs.usgs.gov/sir/2007/5250/pdf/SIR2007-5250.pdf>

Coastal Plain have depths to the bottom of the well screen of 50 feet from the land surface or less. As a means of comparing the relevance of the PRZM-GW conceptual model, EFED has compared the parameterization of the Delmarva corn groundwater scenario to the wells included in this analysis. The Delmarva Corn scenario most closely represents the Virginia Coastal Plain spatially and characteristically. In the Delmarva Corn scenario, the vadose zone ends and the aquifer begins 9 meters (29.5 feet) below the land surface. In the USGS study, it is reported that 26 of 29 Virginia Coastal Plain counties have at least one domestic well with a depth to the bottom of the well screen of 30 feet or less. Using this example, it follows that modeling with PRZM-GW provides EDWCs that represent a subset of a broadly distributed population relying on shallow, private drinking water wells.

Taken together, these publications suggest that vulnerable groundwater used as source drinking is an exposure route that represents some percentage of the U.S. population and is well represented by PRZM-GW modeling.

Risk Assessment Outcomes

With four chemicals (chemicals 5, 7, 16, and 40) where Tier 2 refinement were considered, the risk assessment conclusions did not change based on the additional refinements. In addition, drinking water exposure was the primary contributor to the overall all risk concerns as shown in **Table 3.3**.

Table 3.3. Risk Assessment and Risk Management Outcome Summary

Assessment	Drinking Water Percent Chronic PAD	Food Percent Chronic PAD	Cancer ¹ Water	Cancer ¹ Food	Risk Management Outcome
Chemical 5	-	-	2.5×10^{-5}	1.5×10^{-6}	Registration withdrawn
Chemical 7	-	-	6.2×10^{-6}	3.4×10^{-7}	Number of yearly application was not increased
Chemical 7 (mitigation)	-	-	6.2×10^{-7}	3.4×10^{-7}	
Chemical 16	80	30	8.3×10^{-6}	2.0×10^{-6}	Process not complete to date
Chemical 40	7235	<1	8.6×10^{-2}	-	Process not complete to date
1. Cancer risk threshold defined at 3.0×10^{-6}					

3.3 SUMMARY

In summary, no additional environmental fate parameters such as subsurface transformation or sorption were considered in Tier 2 simulations as these data were not available for the assessed chemicals. However, potential transformation or sorption processes not considered at the Tier 1 level were examined. Data that may be useful for future Tier 2 assessments were identified, and while these data are not typically captured by the standard OCSP guideline requirements, such data may be available in the scientific literature or could be submitted to the EPA for review and consideration in a refined PRZM-GW modeling approach if necessary.

No new scenarios were developed; however, sites for future scenario development were identified and additional characterization of the six standard PRZM-GW scenarios were provided in terms of the potential represented population and spatial relationship.

PRZM-GW represents a significant modeling advancement in that it provides options for characterization and refinement of modeled EDWCs. Beyond providing spatial and temporal context to predicted EDWCs and the ability to evaluate alternate input assumptions, the model allows for robust analysis of the potential down gradient impacts of pesticide applications from a treated field.

4. COMPARISON OF ESTIMATED DRINKING WATER CONCENTRATIONS FROM PRZM-GW AND SCI-GROW MODELS

This chapter compares the results of the Tier 1 model, SCI-GROW, used by the Office of Pesticide Programs (OPP) exclusively through 2012 with PRZM-GW results. This chapter describes the models, methods, and the results of this comparison.

4.1 BACKGROUND

During the one-year evaluation period following the implementation of PRZM-GW as a standard tool in tiered drinking water exposure assessments, concerns were expressed over the difference between PRZM-GW and SCI-GROW estimated pesticide concentrations. To address this concern a systematic comparison of estimated drinking water concentrations (EDWCs) was completed. The methods and the results of this analysis are presented below.

4.2 METHOD OVERVIEW

EDWCs for 77 theoretical pesticides were estimated using PRZM-GW (version 1.01, December 11, 2012) and SCI-GROW (version 2.3, August 8, 2003). For the PRZM-GW simulations, all six current standard scenarios were used.¹⁹ An application rate of 1 kg a.i./ha (0.89 lb a.i./A) was used in all simulations. Although the model input parameter guidance for PRZM-GW and SCI-GROW are different (differences are summarized in **Table 4.1**), the same input values [aerobic soil metabolism half-life and sorption coefficient (K_{oc})] were used for both models in this analysis. Since SCI-GROW was developed assuming a linear adsorption coefficient normalized for soil organic carbon content and does not have the capability to consider K_d values, K_{oc} values were only used in this analysis. The input values used in the model simulations are tabulated in **APPENDIX B**. Sorption input values ranged from one to 10,000 mL/g_{oc}, while the aerobic soil metabolism half-life values ranged from one to 1,000 days.

Table 4.1. Current Model Input Parameter Guidance Comparison

Input Parameter	PRZM-GW ^a	SCI-GROW ^b
Aerobic Soil Metabolism	<p>Use aerobic soil metabolism half-life adjusted to 25°C; Adjust half-lives from studies conducted at temperatures other than 25°C to values at 25°C using a Q_{10} of 2.</p> <p>If multiple aerobic soil metabolism half-life values are available, enter the 90th percentile confidence bound on the mean of the half-lives adjusted to 25°C.</p> <p>If a single aerobic soil metabolism half-life value is available, enter 3x the half-life adjusted to 25°C.</p> <p>If no aerobic soil metabolism data are available, assume that the compound is stable to biodegradation under these conditions, <i>i.e.</i>, enter zero (0).</p>	<p>If three or fewer aerobic soil metabolism half-life values are available, use the mean value. If there are four or more half-lives available, use the median value. If there is more than a five-fold difference, make note of the range.</p>
Sorption Coefficient	If sorption is correlated with organic carbon content, use the K_{oc} values. If sorption is not	If the partition coefficients normalized for organic carbon

	<p>correlated with organic carbon content, use the K_d values. Use the mean of the K_{OC} or K_d values</p> <p>Sorption is correlated with organic carbon content if the coefficient of variation (<i>i.e.</i>, the standard deviation divided by the mean) for K_{OC} values is less than that for K_d values.</p> <p>Use of the mean K_{OC} may not be appropriate for certain chemicals with binding not correlated with organic carbon content, such as those that are ionic at environmental pH values. In these cases, the model user should document the rationale for the selected model input values. Additional guidance may be sought at the EFED WQTT.</p>	<p>content (K_{OC} or K_{FOC}) show greater than a three-fold variation, use the lowest value. If not, then use the median value. SCI-GROW was developed using K_{OC} values ranging from 32-180 mL g_{OC}^{-1} and half-lives from 13-1000 days. Extrapolation beyond these values will increase the uncertainty of the ground water concentration. (The model will not use K_{OC} values > 9995 mL g_{OC}^{-1}.)</p>
<p>a. U.S. Environmental Protection Agency, Office of Pesticide Programs, Environmental Fate and Effects Division, <i>Guidance for Selecting Input Parameters for Modeling Pesticide Concentrations in Groundwater Using the Pesticide Root Zone Model</i>, Version 1.0, October 15, 2012</p> <p>b. U.S. Environmental Protection Agency, Office of Pesticide Programs, Environmental Fate and Effects Division, <i>Input Parameter Guidance</i> (Version 2.1), October 22, 2009. Environmental Fate and Effects Division (EFED) Water Quality Technical Team (WQTT)</p>		

Since the output of SCI-GROW represents the 90-day average high concentration following one year of pesticide applications, a similar application scenario was simulated (*i.e.*, one year of pesticide application once every seven years) for a 100 years using PRZM-GW. The 90-day average high concentrations were determined for each PRZM-GW simulation. An application retreatment interval of seven years was selected for the PRZM-GW simulations to eliminate the potential overlap of applications in the soil profile following multiple sequential years of pesticide application to access the variability in concentrations due to the weather. An application date of June 1 was used for all PRZM-GW simulations.

As part of the evaluation of PRZM-GW, 66 chemicals with monitoring data were used to examine the suitability of using PRZM-GW as a Tier 1 screening-level risk assessment tool. These are the same 66 chemicals that were used in the original evaluation of PRZM-GW.³ These chemicals were also detected in groundwater by NAWQA and included in this analysis regardless of the frequency of detections (50 of these compounds had 5 or more detections). The same analysis described above was completed for 60 of the 66 chemicals. Six chemicals were excluded from this analysis because batch equilibrium data showed that sorption was not correlated to organic carbon content of the soil. Both the SCI-GROW and PRZM-GW 90-day average high concentrations were compared to the peak measured concentrations from the USGS National Water Quality Assessment (NAWQA) Program database.

4.3 RESULTS AND DISCUSSION

Theoretical Chemical Analysis

The PRZM-GW and SCI-GROW estimated concentrations are tabulated in **APPENDIX C (Table C.1.)**, and the results are graphically presented in **Figure 4.1** and **Figure 4.2**. The two

graphs depict the same data; however, the results are binned by K_{oc} values in Figure 4.1 and by aerobic soil metabolism in Figure 4.2.

This analysis confirmed that if a $K_{oc} > 9,995 \text{ mL/g}_{oc}$ (*i.e.*, $10,000 \text{ mL/g}_{oc}$) is used as an input value for SCI-GROW, an output value is provided but it represents a lower bound value based on the rate of application. The reported concentration is the same no matter what aerobic soil metabolism half-life input value is used. When an aerobic soil metabolism half-life value of 1 day is considered, the SCI-GROW concentration is higher when a K_{oc} input value of $10,000 \text{ mL/g}_{oc}$ is used compared to when $5,000 \text{ mL/g}_{oc}$ is used.

Depending on the aerobic soil metabolism half-life value and sorption coefficient, the SCI-GROW estimated concentrations fall within the range of PRZM-GW estimated concentrations. The relationship of SCI-GROW estimated concentrations to the range of PRZM-GW estimated concentrations is cyclic. For example, for a given K_{oc} value, the SCI-GROW estimates are higher than the range of PRZM-GW concentrations for more persistent chemicals; however, as the persistence decreases, the SCI-GROW estimated concentration falls within the range of PRZM-GW estimated concentrations. For the least persistent chemicals, the SCI-GROW estimated concentrations are less than the range of PRZM-GW estimated concentrations.

Table 4.2 highlights the number of times SCI-GROW concentrations are greater than PRZM-GW estimates and how often PRZM-GW estimates are greater than SCI-GROW. This analysis suggests that the SCI-GROW estimated concentrations are the most similar to PRZM-GW estimate concentrations, resulting from the median of the six scenarios. The input values used in simulations, where the PRZM-GW 90-day average high concentration across all scenarios is more than 10x lower than the SCI-GROW estimate concentration, are provided in **Table 4.3**.

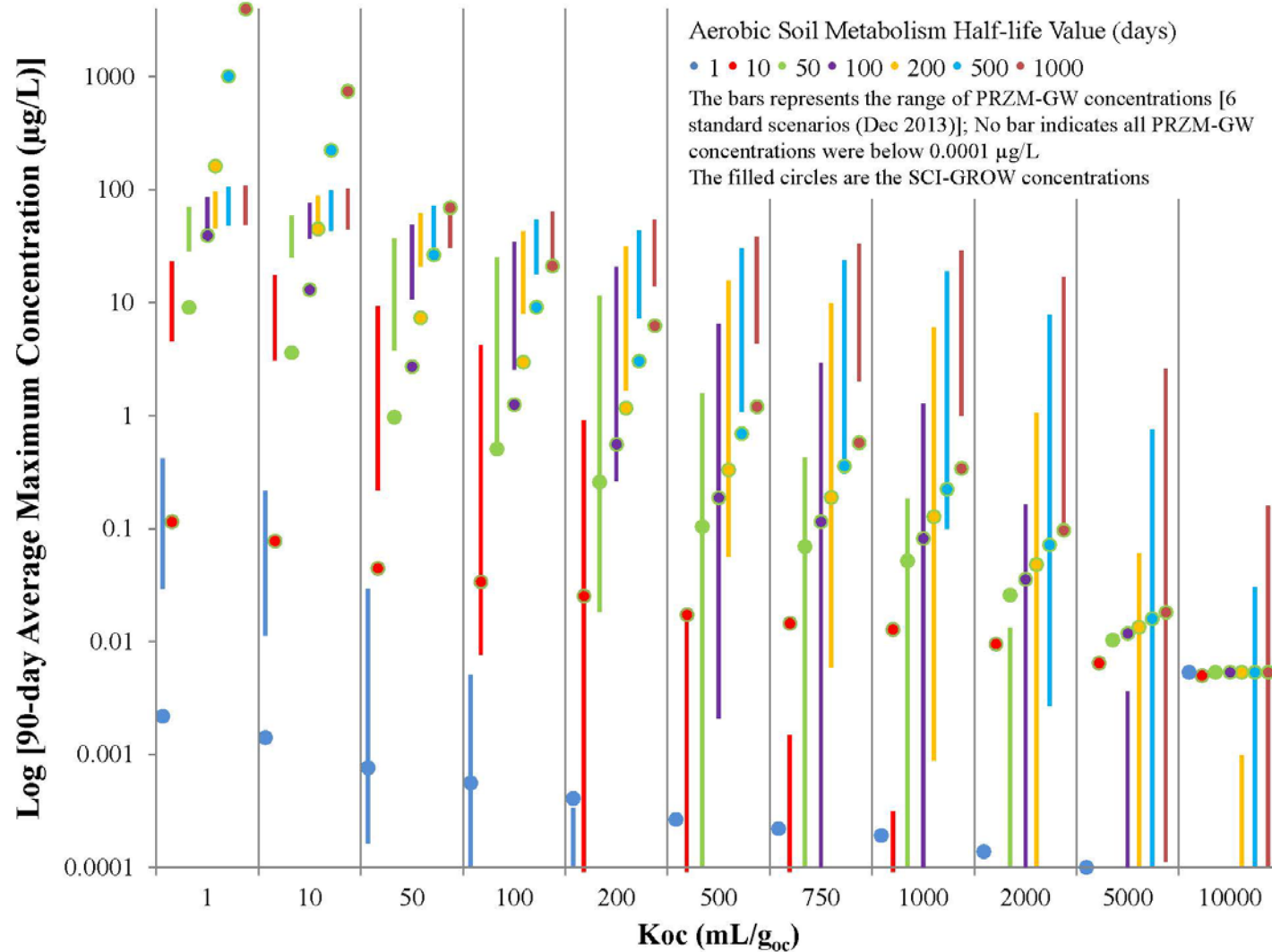


Figure 4.1. PRZM-GW and SCI-GROW Model Estimated Concentrations: Sorption Factor Analysis

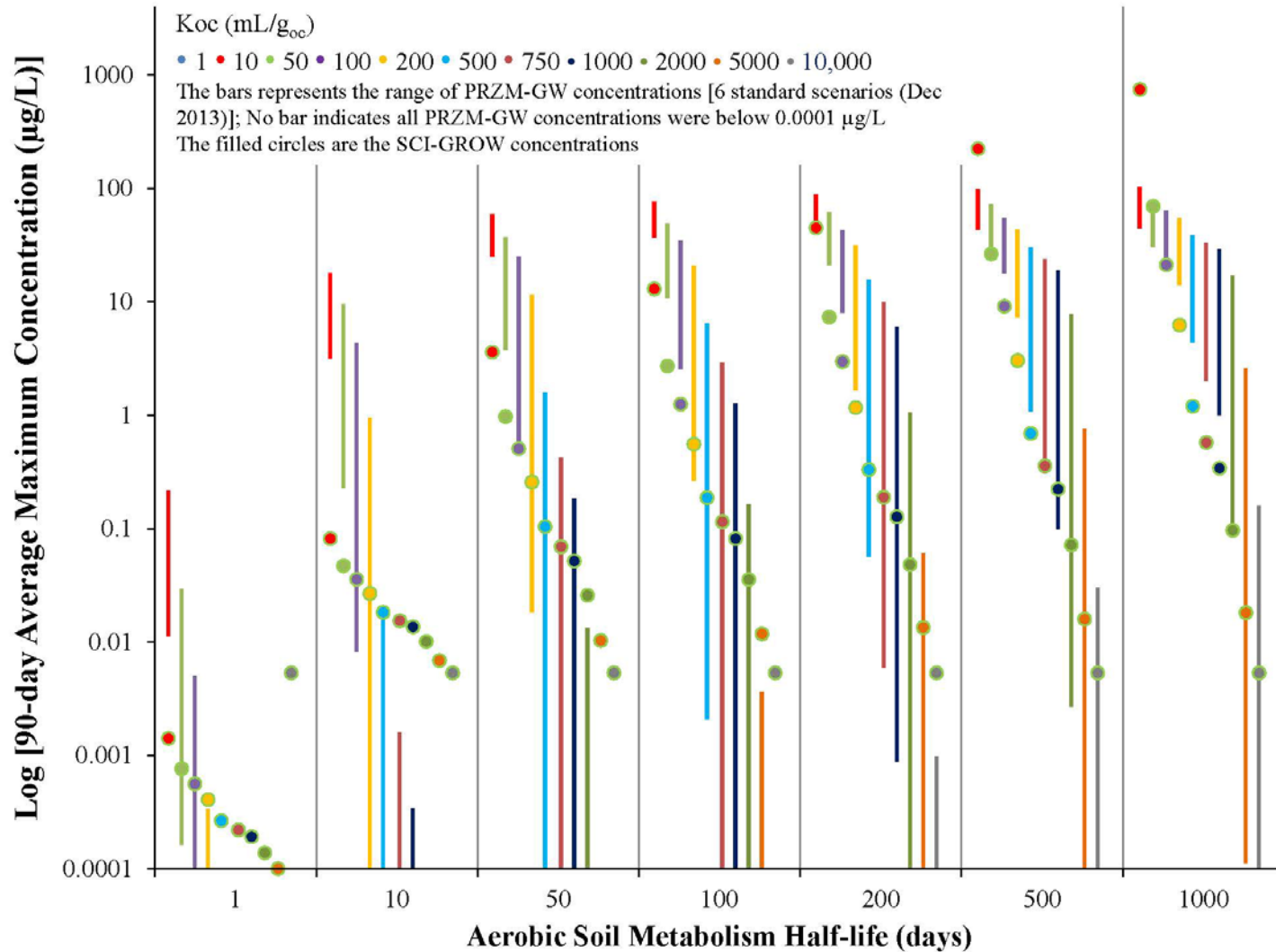


Figure 4.2. PRZM-GW and SCI-GROW Model Estimated Concentrations: Aerobic Soil Metabolism Half-life Analysis

Table 4.2. Comparison of PRZM-GW and SCI-GROW Estimated Concentrations

Metric	Minimum PRZM-GW Scenario	Median PRZM-GW Scenario	Maximum PRZM-GW Scenario
[SCI-GROW] / [PRZM-GW]			
Total Overestimations	52	32	22
≥ 10x Overestimations	34	18	9
≥ 100x Overestimations	19	6	2
≥ 1000x Overestimations	2	0	0
[PRZM-GW] / [SCI-GROW]			
Total Underestimations	25	45	55
≥ 10x Underestimations	3	27	37
≥ 100x Underestimations	0	2	9
≥ 1000x Overestimations	0	0	0
a. Includes all 77 theoretical chemicals.			

Table 4.3. Comparison of PRZM-GW and SCI-GROW Estimated Concentrations

Sorption Coefficient (mL/g _{oc})	Aerobic Soil Metabolism Half-life Value (day)	Magnitude Difference
[SCI-GROW] / [PRZM-GW]		
10000	1	10x
1000	10	100x
2000	10	100x
5000	10	10x
10000	10	10x
5000	50	100x
10000	50	10x
10000	100	10x
1	1000	10x

Evaluation Chemical Analysis

The maximum and minimum PRZM-GW and the SCI-GROW 90-day average concentrations for the 60 chemicals assessed are compared with NAWQA detections in **Figure 4.3** (binned by persistence) and **Figure 4.2** (binned by mobility). The persistence classification used to bin the results shown in these figures does not capture hydrolysis, which may have been considered as part of the PRZM-GW modeling. The range of PRZM-GW estimated concentrations and SCI-GROW estimated concentrations tend to be higher than the NAWQA detection, particularly for more mobile compounds. For less mobile chemicals, the reverse is true.

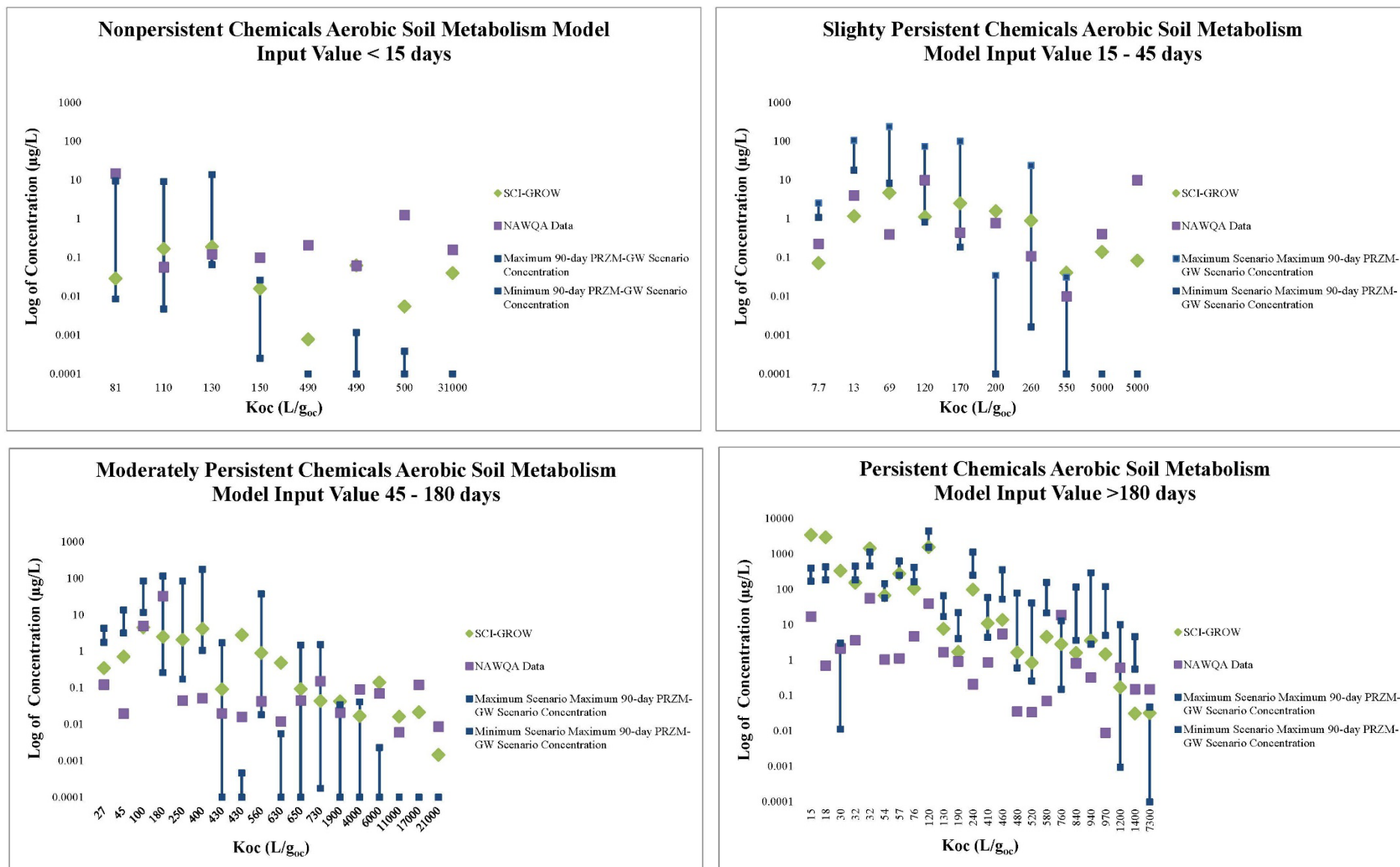


Figure 4.3. PRZM-GW and SCI-GROW Model Estimated 90-day Concentrations Compared with NAWQA Data by Chemical Persistence (based on Aerobic Soil Metabolism Input) Value and Chemical Mobility

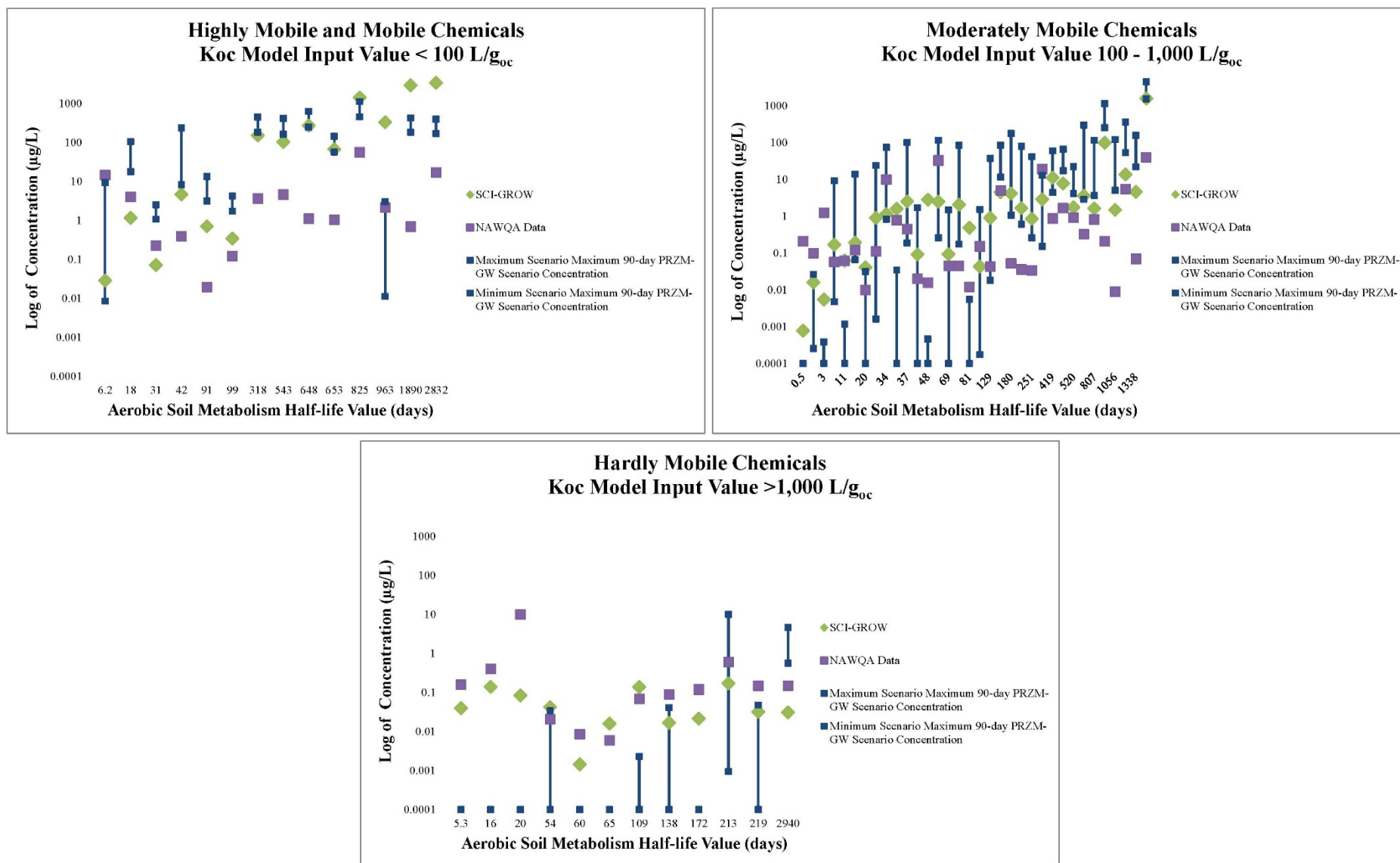


Figure 4.4. PRZM-GW and SCI-GROW Model Estimated 90-day Concentrations Compared with NAWQA Data by Chemical Mobility and Chemical Persistence (based on Aerobic Soil Metabolism Input)

For PRZM-GW simulations, hydrolysis is a very sensitive parameter. For this analysis, hydrolysis was only an input value for PRZM-GW. The figures above do not consider hydrolysis as part of the persistence classification; however, since PRZM-GW considers hydrolysis and hydrolysis does have a large impact on the estimated concentrations, hydrolysis was considered as part of a secondary evaluation for those chemicals²² where hydrolysis is expected. In this analysis, hydrolysis was considered in the PRZM-GW modeling, and hydrolysis was included in the persistence classification used to graphically display the results shown in **Figure 4.5**.

This analysis showed that when hydrolysis is included in PRZM-GW modeling, the maximum 90-day concentration for all the scenarios was less than the measure concentration for seven of the ten chemicals. For the three chemicals where the maximum 90-day PRZM-GW concentration was higher than the measured concentration, the SCI-GROW estimated concentration was within the range of the PRZM-GW estimated concentration. Since the actual use that resulted in the measured concentration is unknown for some of these compounds, the reason for the PRZM-GW underestimation cannot be determined. Examination of the modeled sorption values for all but two of the chemicals would be considered mobile to moderately mobile. In general, based on the model, the persistence of these compounds would not be expected to pose a groundwater concern; therefore, it is likely that these compounds reached the groundwater through mechanisms not represented in the PRZM-GW modeling. For example, the simulated use scenario does not represent the actual use that resulted in the measured concentration. For chlorpyrifos, the peak concentration reported in NAWQA is the result of a use (termiticide) that involves direct injection into the subsurface. Because this use is no longer allowed on the label, it is not represented by the simulated use scenarios. This may be the case for the other chemicals; however, additional analysis of the NAWQA data would need to be completed.

²² 10: malathion (acid water), parathion-methyl, carbaryl, disulfoton, iprodione, terbufos, chlorpyrifos, cypermethrin, carbofuran, and metalaxyl

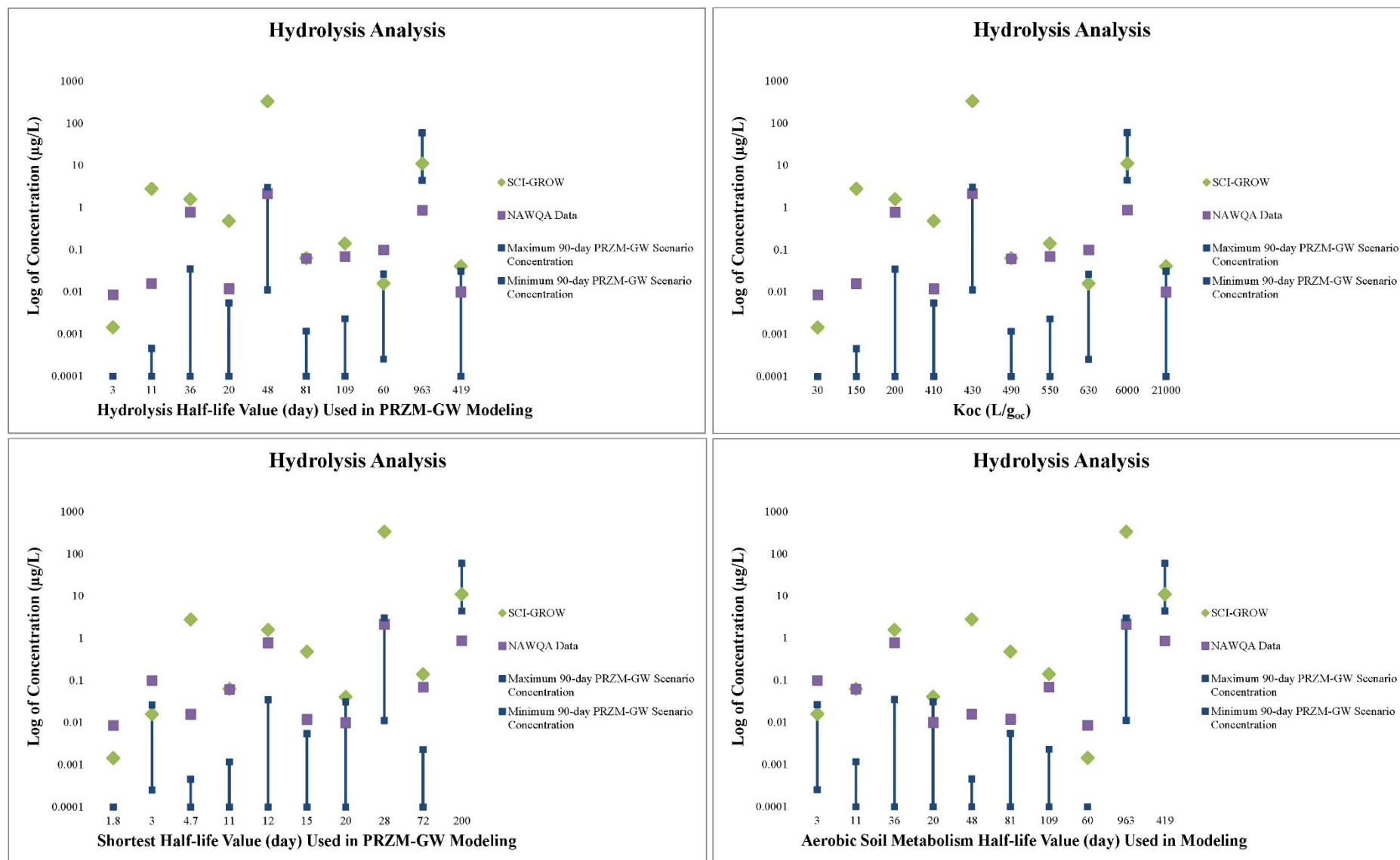


Figure 4.5. Hydrolysis Analysis: PRZM-GW and SCI-GROW Model Estimated 90-day Concentrations Compared with NAWQA Data

5. PRZM-GW MODEL EVALUATION USING GROUNDWATER MONITORING DATA AND UPDATED STANDARD SCENARIOS

5.1 BACKGROUND

There are currently six standard PRZM-GW scenarios used by the Environmental Fate and Effects Division (EFED) to estimate pesticide concentrations in drinking water. These scenarios were used as part of the evaluation of PRZM-GW as a risk assessment tool; however, during the one-year evaluation period following the implementation of PRZM-GW, an error in the maximum water holding capacity was identified in all but one [*i.e.*, North Carolina Cotton (NCC)] of the June 2013 standard scenarios [Florida Citrus (FLC), Florida Potato (FLP), Wisconsin Corn (WIC), Georgia Peanuts (GAP), and Delmarva Sweet Corn (DEL)].

In the 2013 scenarios, the maximum water holding capacity was set to field capacity; however, the PRZM-GW scenario development guidance specifies that the maximum water holding capacity be set half way between the porosity and field capacity. The scenarios were updated to correct this error. In addition to correcting this error, the available depletion parameter was adjusted to account for the change in the maximum water holding capacity. Calculations for these adjustments are provided in **APPENDIX B**. The scenarios were also updated to include the crop canopy height for the volatility route, which is available in the updated version of PRZM-GW (version 1.07). A summary of the adjustments made to the scenarios is provided in **Table 5.1** and are listed out in the meta data for each of the scenarios.

Table 5.1. Summary of Changes Made to the Standard PRZM-GW Scenarios

Scenario ^a	Maximum Water Capacity ^b		Available Depletion		Crop Height (cm) ^c
	2013 ^d	2014 ^e	2013	2014	2014
DEL	0.059-0.095	0.21-0.25	0.33	0.84	300
NCC	0.093-0.287	0.21-0.32	--	--	122
FLC	0.1-0.24	0.25-0.33	0.90	0.90	450
WIC	0.068-0.088	0.22-0.24	0.70	0.90	300
FLP	0.08-0.19	0.20-0.32	0.65	0.90	30
GAP	0.168-0.281	0.25-0.33	0.33	0.60	45
a. See Footnote 11 ; Old: December 20, 2012; New: December 23, 2013 b. These values are soil horizon specific. For more specific details related to the soil horizon, see the meta data files. The range of values is shown for the top seven horizons.					

- c. This information was needed for the volatility routine (added capability in updated version of PRZM-GW (PRZM-GW 1.07))
- d. Value previously set at field capacity
- e. The reported value is half way between porosity and field capacity (as described in the scenario development guidance)

Although these adjustments are not expected to substantially impact the resulting estimated drinking water concentrations (EDWCs) or the utility of PRZM-GW as a screening level risk assessment tool as concluded in the NAFTA Final Report, an evaluation is warranted. The impact of the scenario updates was investigated by comparing the PRZM-GW estimated concentrations to both non-targeted monitoring data, exactly the same as what was done in the NAFTA Final Report (**Chapter 4**).

5.2 METHOD OVERVIEW

The methods used in this updated analysis are exactly the same as previously reported. (See the NAFTA Final Report Chapter 4). In summary, non-targeted monitoring data were used to evaluate the screening abilities of PRZM, and more targeted monitoring data were used to test the refinement capabilities of PRZM.

The following large-scale multi-site monitoring studies were used in this evaluation:

- The National Water Quality Assessment (NAWQA) Program (US Geological Survey)
- The Acetochlor Registration Partnership (ARP) Midwest Corn Production Area (MwCPA) Monitoring Program (also known as the ARP State Ground-Water Monitoring Program)
- The National Alachlor Well-Water Survey (NAWWS) submitted to EPA by Monsanto Company to support alachlor registration.

The fate input values used for each pesticide modeled are provided in **Table 5.2** with all the values provided in **APPENDIX C**. Modeling assumed maximum pesticide application every year, in accordance with the pesticide label for the duration of the simulation unless otherwise noted.

Table 5.2. Range of Fate Parameters Used in the Evaluation

Hydrolysis Half-life	Aerobic Soil Metabolism Half-life	Sorption Coefficient
1.8-300 days 0 (<i>i.e.</i> , stable; n=54)	0.5-2940 days (3x; n=16)	7.7-30820 (K_{oc}) 0.12-7.6 (k_d)

The model was run for each pesticide using each of the six standard scenarios. Model runs were completed in batches where every chemical was run through every scenario for 30 and 100-year simulations. The output was post-processed in Microsoft Excel 2013 to efficiently complete the analyses. Graphical outputs were developed using SigmaPlot (version 12.0).

Results and Discussion

National Water Quality Assessment (NAWQA) Program

The maximum PRZM-GW simulated pesticide concentrations were above the maximum reported concentration for most chemicals across the six simulated standard scenarios (**Figure 5.1**) using either the 30- or 100-year simulation. When the 30-year simulation had incomplete throughputs, the results from the 100-year simulation were reported in this document as the “hybrid” approach. For some chemicals, the ratio of the model predicted concentrations to the highest detected concentration reported in the NAWQA data set was $>100\times$. The majority of the chemicals that PRZM-GW predicted as having higher ($>100\times$) concentrations than the reported concentration were persistent to very persistent (half-life values ranging from >100 days) and were lower-sorbing compounds ($K_{oc} < 400$ mL/g_{oc}). Chemicals with these characteristics are expected to leach to groundwater; therefore, it is important not to underestimate the concentration of these chemicals in groundwater.

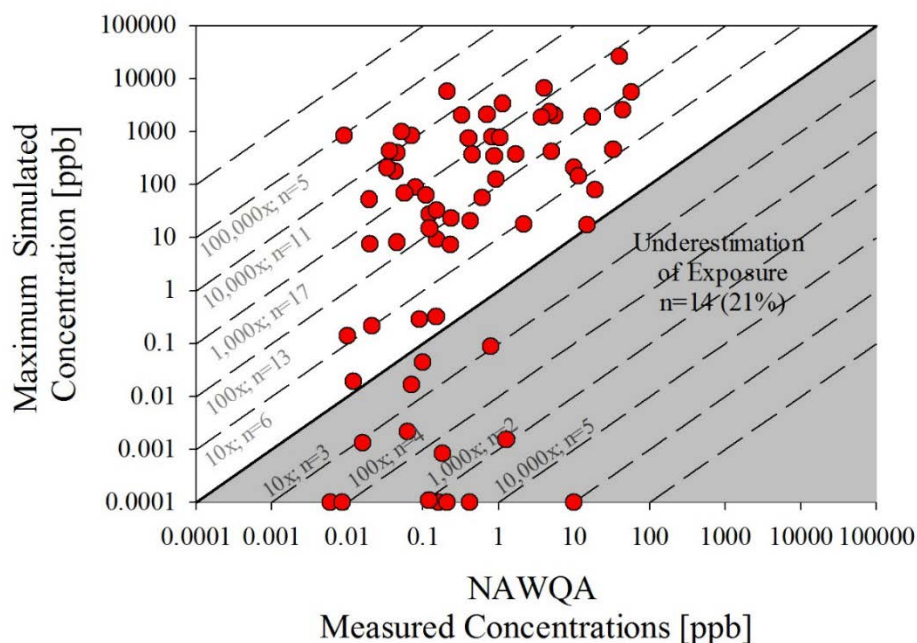


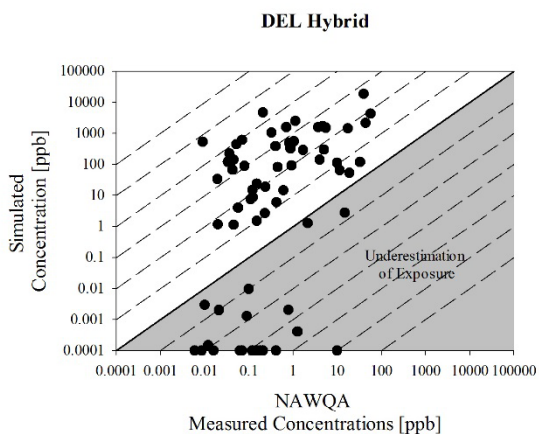
Figure 5.1. Highest PRZM-simulated Concentrations (of all six standard scenarios) Compared with the Highest NAWQA Detections

For several chemicals, the NAWQA dataset concentrations were greater than those predicted by PRZM-GW.²³ Of the 66 pesticides in the NAWQA dataset, 14 peak pesticide detections were higher than those estimated using PRZM-GW, considering the peak simulated concentration from all the standard scenarios (for 30- or 100-year simulations²⁴) as shown in **Figure 5.1**. The number of chemicals PRZM-GW simulated concentrations that were lower than the observed concentrations across the six standard scenarios ranged from 14 to 30 (**Figure 5.2**). Most of the

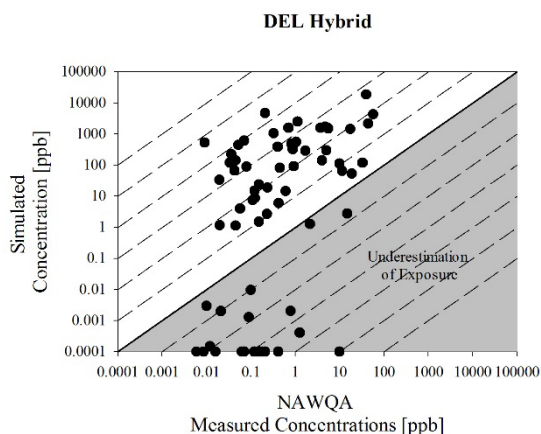
²³ Benfluralin, cypermethrin, triallate, iprodione (most), parathion, chlorpyrifos (most), ethafluralin, glyphosate, propyzamide, carbaryl, dichlobenil, bentazon.

²⁴ When breakthrough was not observed (throughputs <1) for a 30-year simulation, a second simulation was completed for 100 years. This is referred to as the “hybrid” approach.

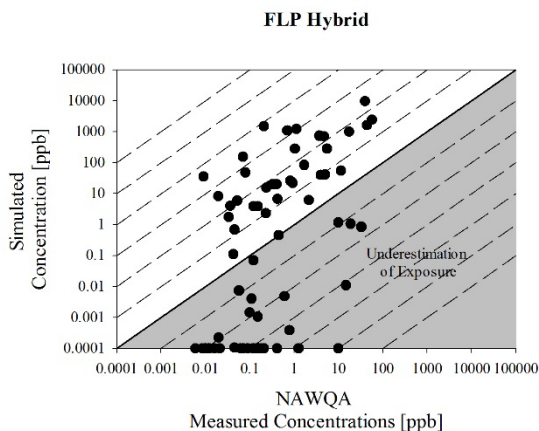
a.



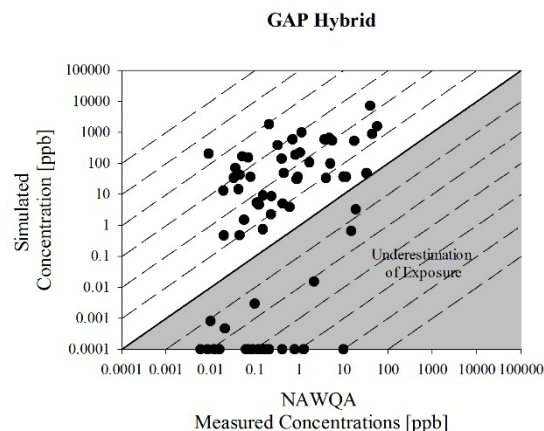
b.



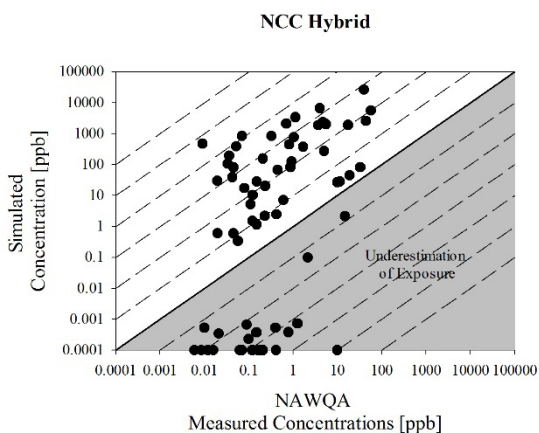
c.



d.



e.



f.

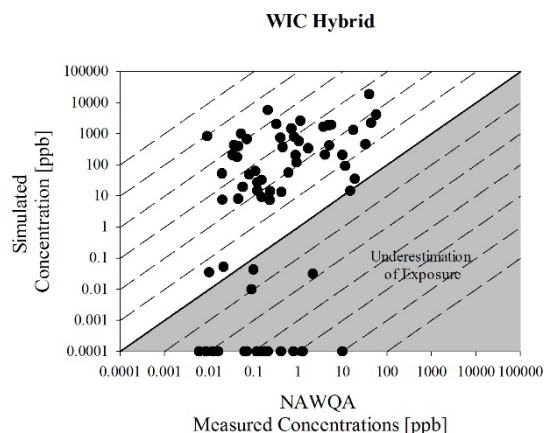


Figure 5.2. PRZM-simulated Concentration (for 30 or 100 years) and Highest NAWQA Reported Detection Log-Log Scale Plots for the Six Standard Scenarios; The solid line is the 1:1 line of predicted versus observed. (PRZM-GW-simulated values less than 0.0001 ppb are reported as 0.0001 ppb for graphical purposes).

PRZM-GW predictions that were lower than the observed detections were from the North Carolina cotton (n=22) and Florida potato (n=30) scenarios. This analysis highlights the difference in the vulnerability of the standard scenarios and is consistent with previous analyses.

Additional analysis of the simulated peak concentrations compared to the NAWQA dataset was completed, looking at the aerobic soil metabolism half-life and mobility input values used in simulations as shown in **Figure 5.3** and **Figure 5.4**, respectively. In general, the majority of these low simulated concentrations were for chemicals with high sorption coefficients ($K_{oc} > 1000 \text{ mL/g}_{oc}$) and low persistence (aerobic soil metabolism half-life values < 30 days). Generally, these chemicals do not leach to groundwater. It is likely that these chemicals reached groundwater through mechanisms that PRZM-GW does not consider (*i.e.*, preferential flow, particle transport, or misuse).

The results are similar to those previously reported. The only noted differences are that use of the updated scenario slightly reduces the number of PRZM-GW over estimations for compounds classified as moderately mobile and slightly mobile (**Table 5.3**) and for the compounds classified as moderately persistent (**Table 5.4**).

In summary, comparison of the NAWQA dataset with PRZM-GW estimated pesticide concentrations, using the updated standard scenarios, indicate that PRZM-GW still conservatively estimates pesticide concentrations for the majority of the chemicals evaluated. Nevertheless, some NAWQA detections are not captured by PRZM-GW model estimates. PRZM-GW was also observed to have a sufficiently protective buffer against underestimating ($>100x$) pesticide concentrations for some chemical detections reported in the NAWQA dataset. Therefore, based on this evaluation, use of the updated standard PRZM-GW scenarios meets the quality objectives by conservatively predicting the occurrence of pesticides in groundwater when conservative input assumptions are made for the majority of chemicals evaluated.

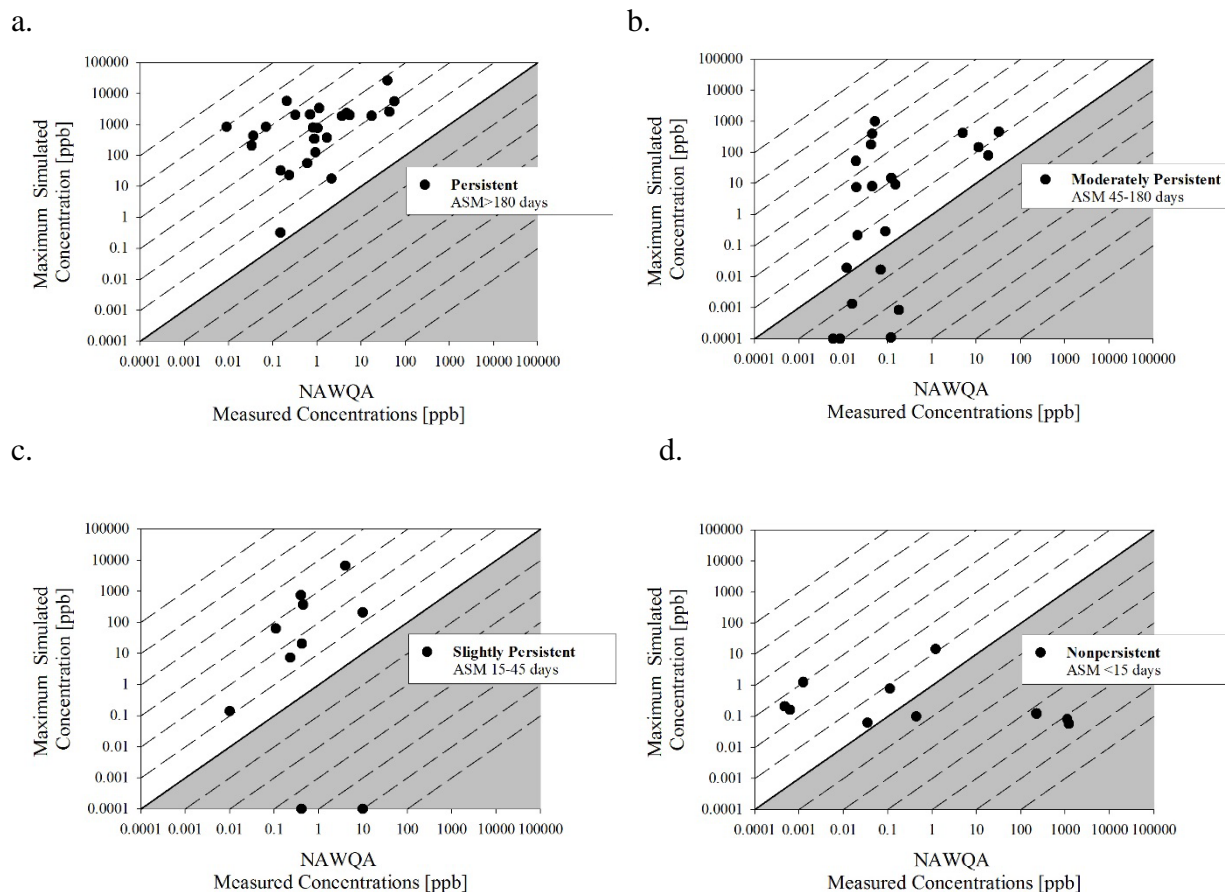


Figure 5.3. Microbial Mediated Persistence Analysis: PRZM-GW-simulated Concentration (for 30 or 100 years) and Highest NAWQA Reported Detection Log-Log Scale Plots; The solid line is the 1:1 line of predicted versus observed concentration. (PRZM-simulated values less than 0.0001 ppb are reported as 0.0001 ppb for graphical purposes).

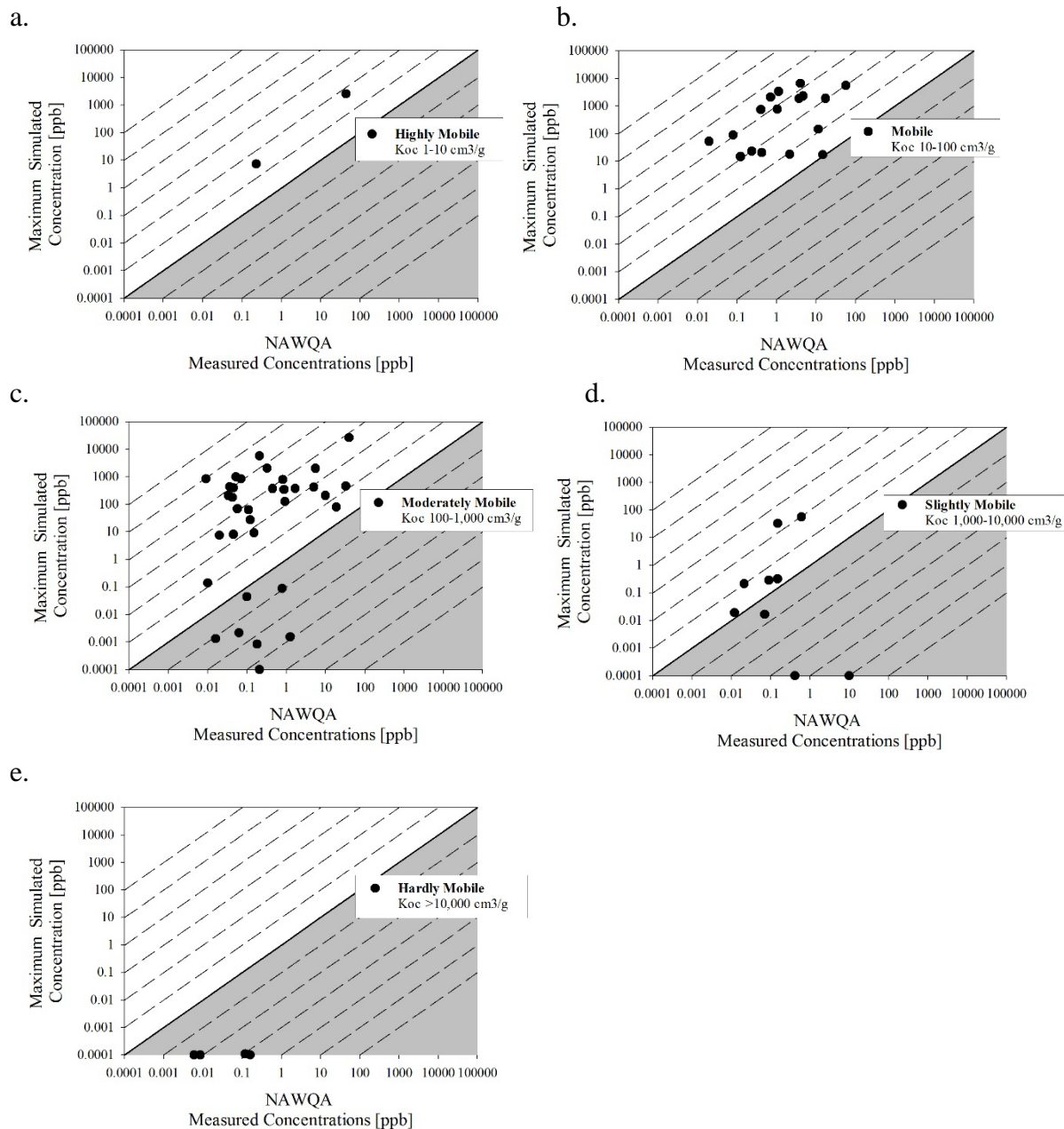


Figure 5.4. Mobility Analysis: PRZM-GW-simulated Concentration (for 30 or 100 years) and Highest NAWQA Reported Detection Log-Log Scale Plots; The solid line is the 1:1 line of predicted versus observed concentrations. (PRZM-GW-simulated values less than 0.0001 ppb are reported as 0.0001 ppb for graphical purposes).

Table 5.3. The Over- and Underestimation of NAWQA Monitoring Data Based on Mobility Classification

Mobility Classification	2013 Scenarios		2014 Scenarios	
	Percent Overestimations	Percent Underestimations	Percent Overestimations	Percent Underestimations
Highly Mobile ($k_{oc} < 10 \text{ cm}^3/\text{g}$)	100	0	100	0
Mobile ($k_{oc} 10\text{-}100 \text{ cm}^3/\text{g}$)	100	0	100	0
Moderately Mobile ($k_{oc} 100\text{-}1,000 \text{ cm}^3/\text{g}$)	85	15	79	21
Slightly Mobile ($k_{oc} 1,000\text{-}10,000 \text{ cm}^3/\text{g}$)	78	22	67	33
Hardly Mobile ($k_{oc} > 10,000 \text{ cm}^3/\text{g}$)	0	100	0	100

Table 5.4. The Over- and Underestimation of NAWQA Monitoring Data Based on Persistence Classification

Aerobic Soil Metabolism Persistence Classification	2013 Scenarios		2014 Scenarios	
	Percent Overestimations	Percent Underestimations	Percent Overestimations	Percent Underestimations
Not Persistent ($t_{1/2} < 15 \text{ days}$)	50	50	50	50
Slightly Persistent ($t_{1/2} = 15 - 45 \text{ days}$)	80	20	80	20
Moderately Persistent ($t_{1/2} = 45\text{-}180 \text{ days}$)	80	20	71	29
Persistent ($t_{1/2} > 180 \text{ days}$)	100	0	100	0

Acetochlor Registration Partnership (ARP) Midwest Corn Production Area (MwCPA) Program

PRZM-GW estimated concentrations were compared to the highest peak and the peak non-point source detection. Site investigations that determined detections were a result of point source contamination and were screened out for acetochlor and atrazine based on an agreement between the ARP and EPA. The agreement stated that detections determined to be a result of point source or intentional contamination by site investigation—further corroborated by EPA—may be excluded from the dataset.

There was generally good agreement between PRZM-simulated pesticide concentrations and observed high-end values from these two Midwestern studies. Short and seven-year concentrations from the MwCPA study and model estimated values for the 2013 and 2014 scenarios are compared in **Table 5.5** for all six of the standard scenarios.

In some cases, the PRZM-GW estimated concentrations are higher (10x) than the observed pesticide concentrations. The highest estimates were observed for atrazine and metolachlor.

Table 5.5. ARP MwCPA Monitoring Maximum Single Detects by Well Site Compared to Predicted Maximum Daily Concentrations for Six Vulnerable 2014 PRZM-GW Scenarios

<i>ARP MwCPA highest individual detection from each well over 7 years of monitoring, (ppb)</i>						<i>PRZM-GW maximum daily concentration from 30-year simulation, 1m screen, (ppb)¹</i>					
<i>Chemical</i>	<i>Max. Single Detect</i>	<i>Max. Single Detect (nps)</i>	<i>3rd highest well</i>	<i>5th highest well</i>	<i>10th highest well</i>	<i>NCC Peak</i>	<i>WIC Peak</i>	<i>DEL Peak</i>	<i>FLC Peak</i>	<i>FLP Peak</i>	<i>GAP Peak</i>
Acetochlor	4.35	0.74	0.74	0.45	0.19	1.5 3.63	27.6 51.5	2.8 35.3	16 32.4	0.07 0.08	5.6 6.1
Alachlor	15.59	15.59	12.84	0.44	0.14	26.9 54	208 304	112 195	132 191	1.2 2.2	37.2 44.8
Atrazine	131.53	7.76	7.76	2.51	1.72	275 244	426 592	295 288	324 343	41.1 49.9	99.1 106
Metolachlor	5.98	5.98	2.87	2.02	0.21	81.2 119	460 447	120 216	286 403	0.8 1.73	48.4 63.9
nps = non-point source <i>italicized values were estimated using 2013 PRZM-GW scenario</i>											

The concentrations observed in the 3rd, 5th, and 10th highest monitored wells are provided in **Table 5.5** to illustrate the potential variability between the wells. This is likely a reflection of the pesticide use history in the zone of influence as well as the difference in the vulnerability of each well.

Additional (refined) modeling was not completed with the updated scenarios as the results are expected to be similar to those previously presented.

National Alachlor Well-Water Survey (NAWWS)

A comparison of the maximum observed pesticide concentrations in the NAWWS survey and the PRZM-GW simulated pesticide concentration using two different scenarios, Wisconsin corn and North Carolina cotton, are provided in **Table 5.6, 4.9, and 4.10**. The results show that PRZM-GW estimated pesticide concentrations are greater than the observed NAWWS highest one-time sample. Wisconsin corn scenario produces substantially higher concentrations than the North Carolina cotton scenario. This is consistent with previous results.

Table 5.6. Comparison of NAWWS Alachlor Concentrations in Private Domestic Wells to PRZM-GW Simulated Maximum Concentration (ppb)

Study ID. and Measurement Type for Alachlor	Highest Detect	3rd Highest	5th Highest	95th %ile
NAWWS one-time sample	6.19	1.07	0.72	0.00
PRZM-GW WIC peak, 30 years of application (highest)	208 304			
PRZM-GW FLP peak, 30 years of application (lowest)	1.2 2.2			

italicized values were estimated using 2013 PRZM-GW scenario

Table 5.7. Comparison of NAWWS Atrazine Concentrations in Private Domestic Wells to PRZM-GW Simulated Peak Concentration (ppb)

Study ID. and Measurement Type for Atrazine	Highest Detect	3 rd Highest	5th Highest	95th %ile
NAWWS one-time sample	6.72	1.96	1.02	0.05
PRZM-GW WIC peak, 30 years of application (highest)	426 592			
PRZM-GW FLP peak, 30 years of application (lowest)	41 50			

Table 5.8. Comparison of NAWWS Metolachlor Concentrations in Private Domestic Wells to Simulated Peak Concentration (ppb)

Study ID. and Measurement Type for Metolachlor	Highest Detect	3 rd Highest	5th Highest	95th %ile
NAWWS one-time sample	3.81	1.60	0.51	0.00
PRZM-GW WIC peak, 30 years of application (highest)	460 447			
PRZM-GW FLP peak, 30 years of application (lowest)	0.8 1.7			

5.3 SUMMARY

While the adjustments made to the standard scenarios do result in slightly different estimated drinking water concentrations for the pesticides examined, the changes do not affect the utility of PRZM-GW as a screening-level risk assessment tool when used with the updated scenarios.

APPENDIX A. Active Ingredients**Table A.1. Pesticide Active Ingredients Included in the One Year Implementation Evaluation of PRZM-GW**

1. Acetochlor	42. Triticonazole
2. Boscalid	
3. Clethodim	
4. Clomazone	
5. CMNP	
6. Coumaphos	
7. Cyflufenamid	
8. Cyflumetofen	
9. Cyromazine	
10. Dicamba	
11. Dicrotophos	
12. Difenoconazole	
13. Fenamidone	
14. Fluensulfone	
15. Fluoxastrobin	
16. Fluthiacet-methyl	
17. Fluxapyroxad	
18. Fomesafen	
19. Flumetsulam	
20. Forchlorfenuron	
21. Flonicamid	
22. Flutolanil	
23. Halosulfuron-methyl	
24. Hydrogen cyanamid	
25. Ipconazole	
26. Linuron	
27. Mandipropamid	
28. Methoxyfenozide	
29. N-chloroaniline	
30. Novaluron	
31. Penthiopyrad	
32. Pyraclostrobin	
33. Quinoxifen	
34. Saflufenacil	
35. Sedaxane	
36. Spirotetramat	
37. Spiromesefin	
38. Tebuconazole	
39. Tebuthiuron	
40. Telone	
41. Topramezone	

APPENDIX B. Model Input Parameters

Table B.1. PRZM-GW and SCI-GROW Comparative Analysis: Model Input Values for the Theoretical Chemicals

Chemical Identification	Sorption Coefficient	Aerobic Soil Metabolism Half-life (days)	DELMARVA Corn	FLORIDA Citrus	FLORIDA Potato	GEORGIA Peanut	NORTH CAROLINA Cotton	WISCONSIN Corn	SCI-GROW	PRZM-GW Maximum Concentration	PRZM-GW Median Concentration	PRZM-GW Minimum Concentration
1	1	1	1.39E-01	4.20E-01	1.62E-01	3.82E-02	2.95E-02	1.83E-01	2.18E-03	4.20E-01	1.51E-01	2.95E-02
2	10	1	7.15E-02	2.17E-01	3.17E-02	1.67E-02	1.13E-02	1.02E-01	1.41E-03	2.17E-01	5.16E-02	1.13E-02
3	50	1	5.62E-03	2.94E-02	1.62E-04	7.35E-04	4.63E-04	9.91E-03	7.63E-04	2.94E-02	3.18E-03	1.62E-04
4	100	1	4.24E-04	5.03E-03	1.95E-06	7.04E-05	3.11E-05	8.70E-04	5.61E-04	5.03E-03	2.47E-04	1.95E-06
5	200	1	7.57E-06	3.38E-04	4.48E-09	2.02E-06	6.93E-07	1.81E-05	4.08E-04	3.38E-04	4.80E-06	4.48E-09
6	500	1	3.10E-09	1.76E-06	1.87E-13	1.67E-09	5.00E-10	8.59E-09	2.66E-04	1.76E-06	2.39E-09	1.87E-13
7	750	1	4.36E-11	8.13E-08	1.27E-15	3.06E-11	9.03E-12	1.26E-10	2.20E-04	8.13E-08	3.71E-11	1.27E-15
8	1000	1	1.66E-12	6.87E-09	3.25E-17	1.36E-12	4.05E-13	4.91E-12	1.92E-04	6.87E-09	1.51E-12	3.25E-17
9	2000	1	3.38E-16	7.29E-12	0.00E+00	2.29E-16	1.15E-16	1.06E-15	1.38E-04	7.29E-12	2.84E-16	0.00E+00
10	5000	1	0.00E+00	2.48E-16	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.96E-05	2.48E-16	0.00E+00	0.00E+00
11	10000	1	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.34E-03	0.00E+00	0.00E+00	0.00E+00
12	1	10	1.06E+01	2.27E+01	2.38E+01	1.32E+01	4.71E+00	2.04E+01	1.21E-01	2.38E+01	1.68E+01	4.71E+00
13	10	10	7.65E+00	1.56E+01	8.33E+00	9.62E+00	3.19E+00	1.78E+01	8.17E-02	1.78E+01	8.98E+00	3.19E+00
14	50	10	2.30E+00	4.47E+00	2.29E-01	2.15E+00	8.26E-01	9.51E+00	4.70E-02	9.51E+00	2.23E+00	2.29E-01
15	100	10	6.74E-01	1.44E+00	8.18E-03	3.80E-01	2.00E-01	4.34E+00	3.57E-02	4.34E+00	5.27E-01	8.18E-03
16	200	10	9.18E-02	2.55E-01	6.42E-05	2.40E-02	1.61E-02	9.45E-01	2.68E-02	9.45E-01	5.79E-02	6.42E-05
17	500	10	1.18E-03	9.92E-03	1.06E-08	1.86E-04	5.83E-05	2.02E-02	1.83E-02	2.02E-02	6.83E-04	1.06E-08
18	750	10	7.90E-05	1.60E-03	1.24E-10	1.05E-05	1.96E-06	8.39E-04	1.54E-02	1.60E-03	4.48E-05	1.24E-10
19	1000	10	8.44E-06	3.40E-04	4.28E-12	8.62E-07	1.30E-07	3.89E-05	1.36E-02	3.40E-04	4.65E-06	4.28E-12
20	2000	10	1.35E-08	3.55E-06	8.60E-16	1.57E-10	8.13E-11	1.14E-08	1.01E-02	3.55E-06	5.78E-09	8.60E-16
21	5000	10	1.18E-13	1.11E-09	0.00E+00	3.40E-18	1.31E-15	1.35E-14	6.86E-03	1.11E-09	7.41E-15	0.00E+00
22	10000	10	5.91E-19	2.44E-13	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.34E-03	2.44E-13	0.00E+00	0.00E+00
23	1	50	5.35E+01	7.00E+01	5.76E+01	3.63E+01	2.86E+01	5.27E+01	9.07E+00	7.00E+01	5.31E+01	2.86E+01
24	10	50	4.61E+01	5.91E+01	3.29E+01	3.08E+01	2.52E+01	4.95E+01	3.60E+00	5.91E+01	3.95E+01	2.52E+01

25	50	50	2.47E+01	3.18E+01	3.76E+00	1.36E+01	1.33E+01	3.69E+01	9.71E-01	3.69E+01	1.92E+01	3.76E+00
26	100	50	1.19E+01	1.76E+01	4.56E-01	7.11E+00	6.03E+00	2.50E+01	5.06E-01	2.50E+01	9.51E+00	4.56E-01
27	200	50	3.43E+00	6.89E+00	1.82E-02	2.49E+00	1.58E+00	1.15E+01	2.58E-01	1.15E+01	2.96E+00	1.82E-02
28	500	50	2.87E-01	1.15E+00	2.78E-05	1.86E-01	9.21E-02	1.57E+00	1.04E-01	1.57E+00	2.37E-01	2.78E-05
29	750	50	5.27E-02	4.23E-01	6.61E-07	3.07E-02	1.27E-02	3.90E-01	6.92E-02	4.23E-01	4.17E-02	6.61E-07
30	1000	50	1.04E-02	1.85E-01	3.41E-08	4.38E-03	2.66E-03	1.14E-01	5.18E-02	1.85E-01	7.39E-03	3.41E-08
31	2000	50	5.88E-05	1.33E-02	1.17E-11	4.89E-06	1.80E-05	1.63E-03	2.58E-02	1.33E-02	3.84E-05	1.17E-11
32	5000	50	2.65E-09	8.46E-05	1.05E-16	4.31E-12	1.20E-09	4.60E-08	1.03E-02	8.46E-05	1.93E-09	1.05E-16
33	10000	50	3.60E-14	1.93E-07	0.00E+00	5.33E-19	1.30E-13	4.38E-14	5.34E-03	1.93E-07	3.99E-14	0.00E+00
34	1	100	6.91E+01	8.57E+01	7.03E+01	4.23E+01	4.53E+01	6.01E+01	3.94E+01	8.57E+01	6.46E+01	4.23E+01
35	10	100	6.18E+01	7.63E+01	4.81E+01	3.71E+01	4.17E+01	5.73E+01	1.30E+01	7.63E+01	5.27E+01	3.71E+01
36	50	100	3.87E+01	4.88E+01	1.07E+01	2.03E+01	2.78E+01	4.58E+01	2.72E+00	4.88E+01	3.33E+01	1.07E+01
37	100	100	2.28E+01	3.07E+01	2.57E+00	1.29E+01	1.71E+01	3.47E+01	1.25E+00	3.47E+01	2.00E+01	2.57E+00
38	200	100	1.00E+01	1.47E+01	2.64E-01	6.21E+00	7.70E+00	2.09E+01	5.56E-01	2.09E+01	8.85E+00	2.64E-01
39	500	100	1.96E+00	3.93E+00	2.08E-03	1.01E+00	1.14E+00	6.47E+00	1.87E-01	6.47E+00	1.55E+00	2.08E-03
40	750	100	6.01E-01	1.89E+00	9.89E-05	2.75E-01	3.06E-01	2.91E+00	1.15E-01	2.91E+00	4.54E-01	9.89E-05
41	1000	100	1.91E-01	1.03E+00	7.98E-06	5.64E-02	9.24E-02	1.28E+00	8.17E-02	1.28E+00	1.42E-01	7.98E-06
42	2000	100	5.53E-03	1.63E-01	6.92E-09	6.98E-04	1.78E-03	7.55E-02	3.55E-02	1.63E-01	3.66E-03	6.92E-09
43	5000	100	1.40E-06	3.60E-03	1.58E-13	3.92E-09	8.17E-07	1.18E-05	1.18E-02	3.60E-03	1.11E-06	1.58E-13
44	10000	100	4.51E-11	2.34E-05	8.37E-18	1.32E-15	2.23E-10	2.73E-11	5.34E-03	2.34E-05	3.62E-11	8.37E-18
45	1	200	7.93E+01	9.63E+01	7.91E+01	4.58E+01	5.93E+01	6.48E+01	1.62E+02	9.63E+01	7.20E+01	4.58E+01
46	10	200	7.25E+01	8.81E+01	6.07E+01	4.09E+01	5.62E+01	6.22E+01	4.50E+01	8.81E+01	6.15E+01	4.09E+01
47	50	200	5.02E+01	6.19E+01	2.11E+01	2.54E+01	4.36E+01	5.15E+01	7.33E+00	6.19E+01	4.69E+01	2.11E+01
48	100	200	3.38E+01	4.28E+01	8.01E+00	1.78E+01	3.37E+01	4.19E+01	2.97E+00	4.28E+01	3.38E+01	8.01E+00
49	200	200	2.01E+01	2.42E+01	1.67E+00	1.07E+01	2.10E+01	3.15E+01	1.17E+00	3.15E+01	2.06E+01	1.67E+00
50	500	200	6.94E+00	9.33E+00	5.63E-02	3.16E+00	6.00E+00	1.56E+01	3.31E-01	1.56E+01	6.47E+00	5.63E-02
51	750	200	3.28E+00	5.57E+00	5.94E-03	1.33E+00	2.39E+00	9.88E+00	1.89E-01	9.88E+00	2.84E+00	5.94E-03
52	1000	200	1.62E+00	3.63E+00	8.88E-04	4.50E-01	1.04E+00	6.07E+00	1.27E-01	6.07E+00	1.33E+00	8.88E-04
53	2000	200	1.63E-01	9.92E-01	3.55E-06	2.87E-02	6.46E-02	1.05E+00	4.82E-02	1.05E+00	1.14E-01	3.55E-06
54	5000	200	1.77E-04	6.02E-02	2.22E-10	6.25E-07	2.29E-04	5.79E-04	1.34E-02	6.02E-02	2.03E-04	2.22E-10

55	10000	200	1.62E-08	9.80E-04	1.47E-14	4.48E-13	1.52E-07	3.33E-09	5.34E-03	9.80E-04	9.77E-09	1.47E-14
56	1	500	8.66E+01	1.05E+02	9.37E+01	4.82E+01	7.11E+01	6.85E+01	1.01E+03	1.05E+02	7.89E+01	4.82E+01
57	10	500	8.03E+01	9.80E+01	7.50E+01	4.36E+01	6.89E+01	6.63E+01	2.24E+02	9.80E+01	7.20E+01	4.36E+01
58	50	500	5.95E+01	7.26E+01	3.41E+01	2.92E+01	6.20E+01	5.81E+01	2.65E+01	7.26E+01	5.88E+01	2.92E+01
59	100	500	4.45E+01	5.39E+01	1.80E+01	2.19E+01	5.44E+01	5.17E+01	9.14E+00	5.44E+01	4.81E+01	1.80E+01
60	200	500	3.34E+01	3.56E+01	7.24E+00	1.58E+01	4.23E+01	4.37E+01	3.04E+00	4.37E+01	3.45E+01	7.24E+00
61	500	500	1.88E+01	1.92E+01	1.09E+00	7.84E+00	2.10E+01	3.03E+01	6.92E-01	3.03E+01	1.90E+01	1.09E+00
62	750	500	1.28E+01	1.41E+01	3.05E-01	5.02E+00	1.27E+01	2.37E+01	3.57E-01	2.37E+01	1.28E+01	3.05E-01
63	1000	500	9.04E+00	1.09E+01	9.95E-02	2.99E+00	8.07E+00	1.90E+01	2.23E-01	1.90E+01	8.56E+00	9.95E-02
64	2000	500	2.67E+00	4.88E+00	2.69E-03	6.08E-01	1.75E+00	7.76E+00	7.17E-02	7.76E+00	2.21E+00	2.69E-03
65	5000	500	1.34E-02	7.56E-01	9.74E-07	5.20E-05	4.93E-02	1.34E-02	1.59E-02	7.56E-01	1.34E-02	9.74E-07
66	10000	500	4.07E-06	3.00E-02	1.17E-10	1.19E-10	1.15E-04	1.91E-07	5.34E-03	3.00E-02	2.13E-06	1.17E-10
67	1	1000	8.95E+01	1.08E+02	9.95E+01	4.93E+01	7.74E+01	7.02E+01	3.98E+03	1.08E+02	8.35E+01	4.93E+01
68	10	1000	8.31E+01	1.02E+02	8.15E+01	4.46E+01	7.60E+01	6.81E+01	7.45E+02	1.02E+02	7.88E+01	4.46E+01
69	50	1000	6.31E+01	7.73E+01	4.10E+01	3.06E+01	7.03E+01	6.12E+01	6.93E+01	7.73E+01	6.22E+01	3.06E+01
70	100	1000	4.94E+01	5.93E+01	2.50E+01	2.35E+01	6.44E+01	5.55E+01	2.12E+01	6.44E+01	5.25E+01	2.35E+01
71	200	1000	4.00E+01	4.13E+01	1.41E+01	1.84E+01	5.47E+01	4.89E+01	6.25E+00	5.47E+01	4.07E+01	1.41E+01
72	500	1000	2.75E+01	2.63E+01	4.40E+00	1.14E+01	3.49E+01	3.85E+01	1.20E+00	3.85E+01	2.69E+01	4.40E+00
73	750	1000	2.18E+01	2.16E+01	2.02E+00	8.79E+00	2.55E+01	3.33E+01	5.76E-01	3.33E+01	2.17E+01	2.02E+00
74	1000	1000	1.80E+01	1.82E+01	1.00E+00	6.64E+00	1.95E+01	2.92E+01	3.41E-01	2.92E+01	1.81E+01	1.00E+00
75	2000	1000	8.61E+00	1.06E+01	8.65E-02	2.18E+00	7.78E+00	1.69E+01	9.65E-02	1.69E+01	8.20E+00	8.65E-02
76	5000	1000	9.23E-02	2.60E+00	1.11E-04	3.91E-04	6.59E-01	4.86E-02	1.81E-02	2.60E+00	7.05E-02	1.11E-04
77	10000	1000	5.13E-05	1.59E-01	2.69E-08	1.77E-09	3.06E-03	1.05E-06	5.34E-03	1.59E-01	2.62E-05	1.77E-09

Table B.2. PRZM-GW Model Input Values for the Evaluation Chemicals

Compound	Hydrolysis t _{1/2} (days)	Aerobic t _{1/2} (days)	Sorption Coefficient	Application Rate (kg/ha)	Initial Application Date	Interval	Number of Applications	Total Rate	Comment
2,4-D	0	6.2	80.5	2.24	20-Apr	7	2	4.48	K _{oc} , mean aerobic soil metabolism
Acetochlor	0	13.3	139	1.68	5-Mar	14	2	3.36	
Alachlor	0	34	123	4.48	5-Mar		1	4.48	
Aldicarb	0	9.64	0.12 (k _d)	3.36	20-Feb		1	3.36	
Atrazine	0	146	100	1.12	1-Apr	14	2	2.24	
Azinphos-methyl	37	95	7.6 (k _d)	2	20-Apr		1	2	
Benfluralin	0	65	10750	3	1-Jun		1	3	
Benomyl	0	3	500	1.68	17-Oct	14	2	3.36	
Bentazon	0	60.7	0.43 k _d	1.12	20-Apr	7	2	2.24	
Bromacil	0	825	32	13.44	20-Apr		1	13.44	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value (275 days)
	0	71.7	247	6.83	4-Apr		1	6.83	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value (23.9 days)
Butylate									Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value
	12	12	198	3	8-Jun	7	3	9	
Carbaryl									
Carbofuran	28	321	30	1.12	1-Jun	14	2	2.24	
Chlorimuron-ethyl	0	91	44.9	0.093	20-Apr	14	3	0.279	
Chlorothalonil	0	16	4957	2.52	15-May	7	7	17.64	

Compound	Hydrolysis t1/2 (days)	Aerobic t1/2 (days)	Sorption Coefficient	Application Rate (kg/ha)	Initial Application Date	Interval	Number of Applications	Total Rate	Comment
Chlorpyrifos	72	109	6040	4.48	15-May	3	8	35.84	
	0	38.4	0.4 (k _d)	0.28	15-May	3	2	0.56	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value (16.8 days)
Clopyralid									
	0	129	562	4.48	1-Mar		1	4.48	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value (43 days)
Cycloate									
Cypermethrin	1.8	60	20800	0.05	1-Jun	7	6	0.3	
Dacthal	0	38.7	5000	10	2-Apr		1	10	
	138	123.3	758	3.36	2-Jan	14	3	10.08	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value
Diazinon									
	0	18	13.4	3.14	15-Apr		1	3.14	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value
Dicamba									
Dichlobenil	0	972	237	22.4	15-Apr		1	22.4	
Dichloroprop	0	42	69	8.43	1-Apr		1	8.43	
Disulfoton	300	20	552	1	1-Jun		1	1	
	0	1116	463	8.96	1-Apr		1	8.96	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to
Diuron									

Compound	Hydrolysis t1/2 (days)	Aerobic t1/2 (days)	Sorption Coefficient	Application Rate (kg/ha)	Initial Application Date	Interval	Number of Applications	Total Rate	Comment
									account for uncertainty in using a single value
EPTC	0	37	172	3	1-Jun	12	4	12	
Ethalfuralin	0	138	3967	1	1-Jun		1	1	
Fipronil	0	128	727	0.3	1-Jun		1	0.3	
Flufenacet	0	48	434	0.78	1-Jun		1	0.78	
Flumetsulam	0	99	27	0.07	1-Jun		1	0.07	
Fluometuron	0	543	75.9	2.24	20-May	30, 14	3	6.72	
Glyphosate	0	5.3	30820	3.73	1-Jun	14	2	7.46	
	0	648	57	8.96	20-May		1	8.96	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value
Hexazinone									Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value, assumed to be K _{oc}
	0	630	17.5	0.56	20-Apr	7	8	4.48	
Imazaquin									
Imazethapyr	0	609	0.49 (k _d)	0.105	1-Apr		1	0.105	
Imidacloprid	0	520	185	0.5	1-Jun		1	0.5	
Iprodione	4.7	48	426	4	1-Jun	14	6	24	PV included unextracted residues
Isofenphos	0	352	972	2	1-Jun	14	2	4	
	0	2940	1368	0.13	1-Apr		1	0.13	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value
Lindane									

Compound	Hydrolysis t _{1/2} (days)	Aerobic t _{1/2} (days)	Sorption Coefficient	Application Rate (kg/ha)	Initial Application Date	Interval	Number of Applications	Total Rate	Comment
Linuron	0	213	2000	1.68	1-Apr		1	1.68	
Malathion	100	3	151	7.84	1-Apr		1	7.84	
Metalaxyl	200	419	409	4.48	1-Apr	3	3	13.44	
Metolachlor	0	49	181	4.48	1-May	14	2	8.96	
Metribuzin	0	318	32	6	20-Apr		1	6	assumed to be K _{OC}
Metsulfuron- methyl	0	31	7.7	0.028	1-Jun	14	2	0.056	
Molinate	0	27	255	3	1-Jun	14	3	9	
Myclobutanil	0	251	224	0.28	1-Jun	14	8	2.24	
Napropamide	0	1338	577	4	20-Apr		1	4	
	0	390	0.14 (k _F)	8.96	1-Aug		1	8.96	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value
Norflurazon	0	189	941	6.72	1-Apr	75	2	13.44	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value
Oryzalin									
Parathion-methyl	40	11	486	0.74	1-Jun	14	4	2.96	
Pebulate	0	180	400	10	1-Jun		1	10	
Pendimethalin	0	172	17040	4	20-Apr		1	4	
Prometon	0	1423	118	67.18	3-Jan		1	67.18	
	0	8.1	112	8.72	3-May		1	8.72	Only one aerobic soil metabolism half-life value is available; therefore, this single value was multiplied by 3 to account for uncertainty in using a single value
Propachlor									

Compound	Hydrolysis t1/2 (days)	Aerobic t1/2 (days)	Sorption Coefficient	Application Rate (kg/ha)	Initial Application Date	Interval	Number of Applications	Total Rate	Comment
Propanil	0	0.5	851	8.96	1-Jun		1	8.96	
Propazine	0	480	125	1.34	1-May		1	1.34	
Propiconazole	0	69	648	0.225	1-Jun	14	4	0.9	
Propyzamide	0	269	841	2	1-Jun	14	2	4	
Tebuthiuron	0	2832	85	4	20-Apr		1	4	assumed to be K _{OC}
Terbacil	0	653	54	2	1-Jun		1	2	
Terbufos	15	81	1448	4	20-Apr		1	4	assumed to be K _{OC}
Thiobencarb	0	246	478	4	20-Apr		1	4	no batch equilibrium data; K _{OC} estimated with EPISUITE using K _{OW} method - highly uncertain
Triallate	0	54	1883	1.5	1-Jun		1	1.5	
Trifluralin	0	219	7300	2	1-Jun	14	2	4	

APPENDIX C. Scenario Updates

Table C.1. Water Holding Capacity Calculations

June 2013													December 2013												
	Horizon Depth (m)	Field Capacity ^a	Min Water	Absolute Difference ^b	Field Capacity Depletion ^c	Bulk Density	Porosity ^d	Field Capacity	Updated Max Water ^e	Absolute Difference ^f	Relative Depletion ^g	Max Water Depletion ^h	Average Depletion Over Rooting Depth ⁱ	Note											
DEL	0-0.1	0.10	0.02	0.07	0.08	1.56	0.41	0.10	0.25	0.23	0.21	0.79													
	0.1-0.2	0.10	0.02	0.07	0.05	1.56	0.41	0.10	0.25	0.23	0.21	0.79													
	0.2-0.4	0.10	0.02	0.08	0.05	1.56	0.41	0.10	0.25	0.24	0.22	0.78													
	0.4-0.6	0.06	0.04	0.02	0.01	1.62	0.39	0.06	0.22	0.18	0.06	0.94													
	0.6-0.8	0.08	0.04	0.04	0.03	1.66	0.37	0.08	0.23	0.19	0.15	0.85													
	0.8-1	0.06	0.02	0.04	0.02	1.68	0.37	0.06	0.21	0.19	0.13	0.87	0.84	maximum rooting depth 100 cm (corn)											
	1-5	0.06	0.02	0.04	0.03	1.63	0.38	0.06	0.22	0.20	0.13	0.87													
	5+																								
	Allowable Depletion From 2012 Scenario = 0.33																								
	R.C.	0-0.1	0.11	0.01	0.10	0.01	1.35	0.49	0.11	0.30	0.29	0.03	0.97												
0.1-0.2		0.10	0.02	0.08	0.01	1.58	0.40	0.10	0.25	0.24	0.04	0.96													
0.2-0.4		0.10	0.02	0.08	0.01	1.58	0.40	0.10	0.25	0.24	0.04	0.96													
0.4-0.6		0.20	0.02	0.19	0.02	1.45	0.45	0.20	0.33	0.31	0.06	0.94													
0.6-0.8		0.10	0.02	0.09	0.01	1.50	0.43	0.10	0.27	0.25	0.03	0.97													
0.8-1		0.24	0.02	0.23	0.02	1.50	0.43	0.24	0.34	0.32	0.07	0.93													
1-5		0.10	0.01	0.09	0.01	1.59	0.40	0.10	0.25	0.24	0.04	0.96	0.96	maximum rooting depth 200 cm (citrus) PR2M max value of 0.9 used as model input value											
5+																									
Allowable Depletion From 2012 Scenario = 0.9																									
R.P.		0-0.1	0.13	0.09	0.04	0.01	1.31	0.51	0.13	0.32	0.23	0.06	0.94												
	0.1-0.2	0.13	0.09	0.04	0.01	1.73	0.35	0.13	0.24	0.15	0.09	0.91													
	0.2-0.4	0.07	0.02	0.05	0.02	1.78	0.33	0.07	0.20	0.18	0.10	0.90													
	0.4-0.6	0.08	0.01	0.07	0.02	1.65	0.36	0.08	0.23	0.22	0.11	0.89	0.91	maximum rooting depth 60 cm (potato) PR2M max value of 0.9 used as model input value											
	0.6-0.8	0.11	0.05	0.06	0.02	1.65	0.38	0.11	0.24	0.19	0.11	0.89													
	0.8-1	0.13	0.04	0.15	0.05	1.75	0.34	0.13	0.26	0.22	0.23	0.77													
	1-5	0.19	0.01	0.18	0.06	1.75	0.34	0.19	0.26	0.26	0.25	0.75													
	5+																								
	Allowable Depletion From 2012 Scenario = 0.85																								
	GA	0-0.1	0.17	0.06	0.10	0.07	1.77	0.33	0.17	0.25	0.19	0.37	0.63												
0.1-0.2		0.17	0.06	0.10	0.07	1.77	0.33	0.17	0.25	0.19	0.37	0.63													
0.2-0.4		0.24	0.11	0.14	0.09	1.76	0.33	0.24	0.28	0.18	0.50	0.50													
0.4-0.6		0.26	0.19	0.07	0.04	1.67	0.37	0.26	0.31	0.12	0.36	0.64	0.60	maximum rooting depth 60 cm (peanut)											
0.6-0.8		0.26	0.19	0.07	0.04	1.67	0.37	0.26	0.31	0.12	0.36	0.64													
0.8-1		0.24	0.17	0.07	0.05	1.67	0.37	0.24	0.31	0.14	0.35	0.65													
1-5		0.28	0.21	0.07	0.05	1.67	0.37	0.28	0.33	0.12	0.42	0.58													
5+																									
Allowable Depletion From 2012 Scenario = 0.33																									
NC		0-0.1	0.09	0.04	0.05	no irrigation	1.78	0.33	0.09	0.21	0.17	no irrigation													
	0.1-0.2	0.09	0.04	0.05	no irrigation	1.78	0.33	0.09	0.21	0.17	no irrigation														
	0.2-0.4	0.22	0.14	0.08	no irrigation	1.75	0.34	0.22	0.28	0.14	no irrigation														
	0.4-0.6	0.24	0.15	0.09	no irrigation	1.66	0.37	0.24	0.31	0.16	no irrigation														
	0.6-0.8	0.28	0.21	0.07	no irrigation	1.74	0.34	0.28	0.31	0.10	no irrigation														
	0.8-1	0.29	0.21	0.08	no irrigation	1.69	0.36	0.29	0.32	0.11	no irrigation														
	1-5	0.28	0.19	0.09	no irrigation	1.75	0.34	0.28	0.31	0.12	no irrigation														
	5+																								
	Allowable Depletion From 2012 Scenario = no irrigation																								
	WI	0.09	0.09	0.05	0.02	1.63	0.38	0.09	0.24	0.20	0.08	0.92													
0.09		0.09	0.05	0.02	1.63	0.38	0.09	0.24	0.20	0.08	0.92														
0.08		0.09	0.05	0.02	1.68	0.37	0.08	0.22	0.20	0.08	0.92														
0.08		0.09	0.05	0.02	1.68	0.37	0.08	0.22	0.20	0.08	0.92														
0.07		0.02	0.05	0.02	1.59	0.40	0.07	0.23	0.22	0.07	0.93														
0.07		0.02	0.05	0.02	1.59	0.40	0.07	0.23	0.22	0.07	0.93														
0.07		0.02	0.05	0.02	1.59	0.40	0.07	0.23	0.22	0.07	0.93	0.92	maximum rooting depth 100 cm (corn) PR2M max value of 0.9 used as model input value												
0.07		0.02	0.05	0.02	1.59	0.40	0.07	0.23	0.22	0.07	0.93														
Allowable Depletion From 2012 Scenario = 0.7																									

a. Previously reported as the max water capacity

b. "Absolute Difference" = "Field Capacity" - "Min Water"

c. Depletion adjustment to account for updated maximum water capacity; "Absolute Difference" x (1 - Allowable Depletion From June 2013 Scenario)

d. Porosity = 1 - ("Bulk Density" / 2.65)

e. "Updated Max Water" = AVERAGE ("Porosity" * "Field Capacity")

f. "Absolute Difference" = "Updated Max Water" - "Min Water"

g. "Field Capacity Depletion" / "Absolute Difference"

h. "Max Water Depletion" = 1 - "Relative Depletion"

i. "Average Depletion Over Rooting Depth" = AVERAGE over Root Depth as specified in note (j.e., used rooting depth from scenario and averaged depletion over the corresponding depth to calculate scenario input value)